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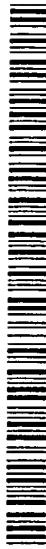
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WO 02/38628 A2

(54) Title: SUBSTITUTED PYRIDYL AMINE LIGANDS, COMPLEXES, CATALYSTS AND PROCESSES FOR POLYMERIZING AND POLYMERS

(57) Abstract: New ligands, compositions, metal-ligand complexes and arrays with pyridylamine ligands are disclosed that catalyze the polymerization of monomers into polymers. Certain of these catalysts with hafnium metal centers have high performance characteristics, including higher comonomer incorporation into ethylene/olefin copolymers, where such olefins are for example, 1-octene, isobutylene or styrene. Certain of the catalysts are particularly effective at polymerizing propylene to high molecular weight isotactic polypropylene in a solution process at a variety of polymerization conditions.

5 SUBSTITUTED PYRIDYL AMINE LIGANDS,
COMPLEXES, CATALYSTS AND PROCESSES FOR
POLYMERIZING AND POLYMERS

10 [0001] This application claims the benefit of U.S. Provisional Patent Application No. 60/246,781, filed November 7, 2000 and the benefit of U.S. Provisional Patent Application No. 60/301,666, filed June 28, 2001, both of which are incorporated herein by reference for all purposes.

15 FIELD OF THE INVENTION

[0002] The present invention relates to ligands, complexes, compositions and/or catalysts that provide enhanced olefin polymerization capabilities based on a substituted pyridyl amine structure and hafnium. The invention also relates to methods of polymerization. The invention also relates to isotactic polypropylene and methods of preparing isotactic polypropylene.

BACKGROUND OF THE INVENTION

[0003] Ancillary (or spectator) ligand-metal coordination complexes (e.g., organometallic complexes) and compositions are useful as catalysts, additives, stoichiometric reagents, monomers, solid state precursors, therapeutic reagents and drugs. Ancillary ligand-metal coordination complexes of this type can be prepared by combining an ancillary ligand with a suitable metal compound or metal precursor in a suitable solvent at a suitable temperature. The ancillary ligand contains functional groups that bind to the metal center(s), remain associated with the metal center(s), and therefore provide an opportunity to modify the steric, electronic and chemical properties of the active metal center(s) of the complex.

[0004] Certain known ancillary ligand-metal complexes and compositions are catalysts for reactions such as oxidation, reduction, hydrogenation, hydrosilylation,

hydrocyanation, hydroformylation, polymerization, carbonylation, isomerization, metathesis, carbon-hydrogen activation, carbon-halogen activation, cross-coupling, Friedel-Crafts acylation and alkylation, hydration, dimerization, trimerization, oligomerization, Diels-Alder reactions and other transformations.

5 [0005] One example of the use of these types of ancillary ligand-metal complexes and compositions is in the field of polymerization catalysis. In connection with single site catalysis, the ancillary ligand typically offers opportunities to modify the electronic and/or steric environment surrounding an active metal center. This allows the ancillary ligand to assist in the creation of possibly different polymers. Group 4 metallocene 10 based single site catalysts are generally known for polymerization reactions. See, generally, "Chemistry of Cationic Dicyclopentadienyl Group 4 Metal-Alkyl Complexes", Jordan, *Adv. Organometallic Chem.*, 1991, Vol. 32, pp. 325-153 and "Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts", Brintzinger, et al., *Angew. Chem. Int. Ed. Engl.*, 1995, Vol. 34, pp. 1143-1170, and the references 15 therein, all of which is incorporated herein by reference.

[0006] However, those of skill in the art of single site catalysis appreciate that there may be substantial differences in performance between different metal centers. For example, U.S. Patent 5,064,802 discloses a broad category of mono-cyclopentadienyl ligand catalysts with a broad disclosure of useful metals, and U.S. Patent 5,631,391 more 20 specifically discloses that titanium metal centers offer performance advantages with respect to the same or similar ligands. Additionally, Coates, et al., *Angew. Chem. Int. Ed.*, 2000, vol. 39, pp. 3626-3629 describes the unpredictable nature of olefin polymerization catalyst structure-activity relationships. Thus, references that describe, for example, groups 3-13 and the lanthanides, for example in U.S. Patent 6,103,657, are 25 not of adequate performance indicators of all that is within the scope of what is allegedly described. Moreover, as those of skill in the art appreciate, differences in ligand substituents typically polymerize different monomers at different performances under different polymerization conditions, and discovering those specifics remains a challenge.

[0007] One application for metallocene catalysts is producing isotactic polypropylene. 30 An extensive body of scientific literature examines catalyst structures, mechanism and polymers prepared by metallocene catalysts. See, e.g., Resconi et al., "Selectivity in Propene Polymerization with Metallocene Catalysts," *Chem. Rev.* 2000, 100, 1253-1345 and G.W. Coates, "Precise Control of Polyolefin Stereochemistry Using Single-Site

Metal Catalysts," *Chem. Rev.* 2000, 100, 1223-1252 and the references sited in these review articles. See also, U.S. Patent 5,026,798 that reports a mono-cyclopentadienyl metallocene for the production of isotactic polypropylene. Isotactic polypropylene has historically been produced with heterogeneous catalysts that may be described as a

5 catalyst on a solid support (*e.g.*, titanium tetrachloride and aluminum alkyls on magnesium dichloride). This process typically uses hydrogen to control the molecular weight and electron-donor compounds to control the isotacticity. See also EP 0622380, U.S. Patent No. 4,297,465, U.S. Patent No. 5,385,993 and U.S. Patent No. 6,239,236.

[0008] Given the extensive research activities with respect to metallocene catalysts, there 10 is continued interest in the next generation of non-cyclopentadienyl ligands for olefin polymerization catalysts providing attractive alternatives. See, *e.g.*, "The Search for New-Generation Olefin Polymerization Catalysts: Life beyond Metallocenes", Gibson, et al., *Angew. Chem. Int. Ed.*, 1999, vol. 38, pp. 428-447; *Organometallics* 1999, 18, pp. 3649-3670. Recently, such systems have been discovered, *see, e.g.*, U.S. 6,103,657 and 15 U.S. 5,637,660. For isotactic polypropylene, bis-amide catalysts have been disclosed in U.S. Patent 5,318,935 and amidinate catalysts have been disclosed in WO 99/05186. See also U.S. Patent 6,214,939.

[0009] There remains a need for the discovery and optimization of non-cyclopentadienyl 20 based catalysts for olefin polymerization, and in particular for certain polymers, such as isotactic polypropylene and ethylene-alpha-olefin copolymers. For a solution polymerization methodology, this need may be acute in view of the lack of versatile catalysts for the preparation of isotactic polypropylene at commercially acceptable temperatures. Indeed, new polymer properties are disclosed herein for isotactic polypropylene, ethylene-styrene copolymers and ethylene-isobutylene copolymers.

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SUMMARY OF THE INVENTION

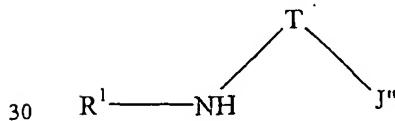
[0010] This invention discloses surprising enhanced catalytic performances for olefin 30 polymerization when certain combinations of ligands and hafnium metal precursors are employed. This invention also discloses surprising enhanced catalytic performances for olefin polymerization when certain metal complexes are employed in a catalyst, including 2,1 metal complexes and 3,2 metal complexes. In addition, some of the ligands employed herein are themselves novel.

[0011] In some embodiments, this invention discloses both the preferred use of a hafnium metal center and certain pyridyl-amine ligands. Such combinations lead to new ligand-metal complexes, catalyst compositions and processes for the polymerization of olefins, diolefins, or other polymerizable monomers. In particular, copolymers of 5 ethylene and another monomer may be prepared with controlled incorporation of the other monomer (e.g., 1-octene, isobutylene, or styrene) into the polymer backbone. In some embodiments, this control is adjusted so that the olefin incorporation is considered to be high with respect to polymers currently known or commercially available. Also in particular, propylene may be polymerized into very high molecular weight isotactic 10 polypropylene. Thus, polymers having novel, improved or desired properties may be prepared using the catalysts and processes of this invention.

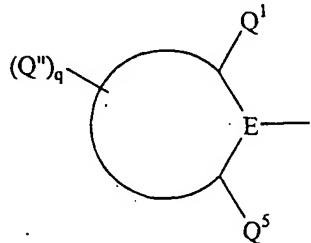
[0012] More specifically, in some embodiments, the use of a hafnium metal has been found to be preferred as compared to a zirconium metal for pyridyl-amine ligand catalysts. A broad range of ancillary ligand substituents may accommodate the enhanced 15 catalytic performance. The catalysts in some embodiments are compositions comprising the ligand and metal precursor, and optionally may additionally include an activator, combination of activators or activator package.

[0013] The invention disclosed herein additionally includes catalysts comprising ancillary ligand-hafnium complexes, ancillary ligand-zirconium complexes and 20 optionally activators, which catalyze polymerization and copolymerization reactions, particularly with monomers that are olefins, diolefins or other unsaturated compounds. Zirconium complexes, hafnium complexes, compositions or compounds using the disclosed ligands are within the scope of this invention. The metal-ligand complexes may be in a neutral or charged state. The ligand to metal ratio may also vary, the exact 25 ratio being dependent on the nature of the ligand and metal-ligand complex. The metal-ligand complex or complexes may take different forms, for example, they may be monomeric, dimeric or higher orders thereof.

[0014] For example, suitable ligands useful in this invention may be characterized by the following general formula:



wherein R^1 is a ring having from 4-8 atoms in the ring generally selected from the group consisting of substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl and substituted heteroaryl, such that R^1 may be characterized by the general formula:



5 where Q^1 and Q^5 are substituents on the ring ortho to atom E, with E being selected from the group consisting of carbon and nitrogen and with at least one of Q^1 or Q^5 being bulky (defined as having at least 2 atoms). Q''_q represents additional possible substituents on the ring, with q being 1, 2, 3, 4 or 5 and Q'' being selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. T is a bridging group selected from the group consisting of $-CR^2R^3-$ and $-SiR^2R^3-$ with R^2 and R^3 being independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, substituted aryl, heteroaryl, substituted heteroaryl, heterocycloalkyl, substituted heterocycloalkyl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. J'' is generally selected from the group consisting of heteroaryl and substituted heteroaryl, with particular embodiments for particular reactions being described herein.

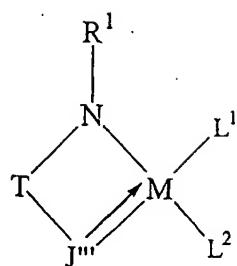
10 [0015] Also for example, in some embodiments, the ligands of the invention may be combined with a metal precursor compound that may be characterized by the general formula $Hf(L)_n$ where L is independently selected from the group consisting of halide (F, Cl, Br, I), alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and optionally two L groups may be linked together in a ring structure. n is 1, 2, 3, 4, 5, or 6.

[0016] In another aspect of the invention, a polymerization process is disclosed for monomers. The polymerization process involves subjecting one or more monomers to the catalyst compositions or complexes of this invention under polymerization conditions. The polymerization process can be continuous, batch or semi-batch and can be homogeneous, supported homogeneous or heterogeneous. Another aspect of this invention relates to arrays of ligands, metal precursors and/or metal-ligand complexes. These arrays are useful for the high speed or combinatorial materials science discovery or optimization of the catalyst compositions or complexes disclosed herein.

[0017] These catalysts comprising ancillary ligand-metal complexes or compositions comprising metal precursors and ligands and, optionally, activators are particularly effective at polymerizing α -olefins (such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and styrene), copolymerizing ethylene with α -olefins (such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and styrene), and copolymerizing ethylene with 1,1-disubstituted olefins (such as isobutylene). These compositions might also polymerize monomers that have polar functionalities in homopolymerizations or copolymerizations. Also, diolefins in combination with ethylene and/or α -olefins or 1,1-disubstituted olefins may be copolymerized. The new catalyst compositions can be prepared by combining a hafnium precursor with a suitable ligand and, optionally, an activator or combination of activators. This invention discloses a novel class of catalysts and improved method for preparing isotactic polypropylene. The catalyst is useful for polymerizing a wide variety of polymerizable monomers.

[0018] In particular, a method of producing isotactic polypropylene is in a solution process is disclosed and is surprisingly tunable. In one aspect, the temperature of the solution polymerization process can be increased, which generally decreases the molecular weight, but surprisingly, while maintaining a relatively high isotacticity of the polypropylene and while maintaining a relatively high melting point for the polypropylene. In another aspect, the temperature of the solution process can be increased without the molecular weight of the polypropylene dropping so low to levels that are unacceptable for certain commercial applications.

[0019] In certain aspects, it has been discovered that certain ligands complex to the metal resulting in novel complexes. In one aspect, the 3,2 metal-ligand complexes of this invention may be generally characterized by the following formula:



where M is zirconium or hafnium;

R¹ and T are defined above;

J''' being selected from the group of substituted heteroaryls with 2 atoms bonded

- 5 to the metal M, at least one of those atoms being a heteroatom, and with one atom of J''' is bonded to M via a dative bond, the other through a covalent bond; and
- L¹ and L² are independently selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and
- 10 optionally the L groups may be linked together in a ring structure.

[0020] In another aspect, a solution process to prepare isotactic polypropylene is provided comprising adding a catalyst and propylene monomer to a reactor and subjecting the contents to polymerization conditions, where the temperature of the solution process is at least 110°C and polypropylene is produced that has a weight average molecular weight of at least 100,000, without a drop off in tacticity value (*i.e.*, crystallinity index).

20 [0021] Thus, it is a feature of this invention to use hafnium-ligand complexes as polymerization catalysts with enhanced performance.

[0022] It is an object of this invention to polymerize olefins and unsaturated monomers with hafnium-ligand complexes. It is also an object of this invention to polymerize olefins and unsaturated monomers with compositions including substituted pyridyl amine ligands and hafnium metal precursors.

[0023] It is still a further object of this invention to polymerize olefins and unsaturated monomers with the hafnium-ligand complexes that additionally comprise an activator or combination of activators.

[0024] It is also an object of this invention to use non-metallocene group 4 complexes as polymerization catalysts for the production of isotactic polypropylene.

[0025] It is a further object of this invention to polymerize olefins and unsaturated monomers with a catalyst comprised of metal complexes comprising 3,2 ligands.

5 [0026] Further objects and aspects of this invention will be evident to those of skill in the art upon review of this specification.

BRIEF DESCRIPTION OF THE DRAWINGS

10 [0027] Figure 1 depicts Table 1, which lists compounds that may be useful for synthesizing the ligands in this invention.

[0028] Figure 2 depicts Table 2, which lists other compounds that may be useful for synthesizing the ligands in this invention.

15 [0029] Figure 3 depicts Table 3, which shows the ligands and results from examples, below, using the Hf metal precursor.

[0030] Figure 4 depicts Table 4, which shows the ligands and results from comparative examples, below, using the Zr metal precursor.

DETAILED DESCRIPTION OF THE INVENTION

20 [0031] The inventions disclosed herein include metal complexes and compositions, which are useful as catalysts for polymerization reactions.

[0032] As used herein, the phrase "characterized by the formula" is not intended to be limiting and is used in the same way that "comprising" is commonly used. The term 25 "independently selected" is used herein to indicate that the R groups, e.g., R¹, R², R³, R⁴, and R⁵ can be identical or different (e.g. R¹, R², R³, R⁴, and R⁵ may all be substituted alkyls or R¹ and R² may be a substituted alkyl and R³ may be an aryl, etc.). Use of the singular includes use of the plural and vice versa (e.g., a hexane solvent, includes hexanes). A named R group will generally have the structure that is recognized in the art 30 as corresponding to R groups having that name. The terms "compound" and "complex" are generally used interchangeably in this specification, but those of skill in the art may recognize certain compounds as complexes and vice versa. For the purposes of illustration, representative certain groups are defined herein. These definitions are

intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

[0033] "Hydrocarbyl" refers to univalent hydrocarbyl radicals containing 1 to about 30 carbon atoms, preferably 1 to about 24 carbon atoms, most preferably 1 to about 12 carbon atoms, including branched or unbranched, saturated or unsaturated species, such as alkyl groups, alkenyl groups, aryl groups, and the like. "Substituted hydrocarbyl" refers to hydrocarbyl substituted with one or more substituent groups, and the terms "heteroatom-containing hydrocarbyl" and "heterohydrocarbyl" refer to hydrocarbyl in which at least one carbon atom is replaced with a heteroatom.

[0034] The term "alkyl" is used herein to refer to a branched or unbranched, saturated or unsaturated acyclic hydrocarbon radical. Suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), vinyl, n-butyl, t-butyl, i-butyl (or 2-methylpropyl), etc. In particular embodiments, alkyls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

[0035] "Substituted alkyl" refers to an alkyl as just described in which one or more hydrogen atom bound to any carbon of the alkyl is replaced by another group such as a halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and combinations thereof. Suitable substituted alkyls include, for example, benzyl, trifluoromethyl and the like.

[0036] The term "heteroalkyl" refers to an alkyl as described above in which one or more hydrogen atoms to any carbon of the alkyl is replaced by a heteroatom selected from the group consisting of N, O, P, B, S, Si, Sb, Al, Sn, As, Se and Ge. This same list of heteroatoms is useful throughout this specification. The bond between the carbon atom and the heteroatom may be saturated or unsaturated. Thus, an alkyl substituted with a heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, or seleno is within the scope of the term heteroalkyl. Suitable heteroalkyls include cyano, benzoyl, 2-pyridyl, 2-furyl and the like.

[0037] The term "cycloalkyl" is used herein to refer to a saturated or unsaturated cyclic non-aromatic hydrocarbon radical having a single ring or multiple condensed rings. Suitable cycloalkyl radicals include, for example, cyclopentyl, cyclohexyl, cyclooctenyl, bicyclooctyl, etc. In particular embodiments, cycloalkyls have between 3 and 200

carbon atoms, between 3 and 50 carbon atoms or between 3 and 20 carbon atoms.

[0038] "Substituted cycloalkyl" refers to cycloalkyl as just described including in which one or more hydrogen atom to any carbon of the cycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted cycloalkyl radicals include, for example, 4-dimethylaminocyclohexyl, 4,5-dibromocyclohept-4-enyl, and the like.

[0039] The term "heterocycloalkyl" is used herein to refer to a cycloalkyl radical as described, but in which one or more or all carbon atoms of the saturated or unsaturated cyclic radical are replaced by a heteroatom such as nitrogen, phosphorous, oxygen, sulfur, silicon, germanium, selenium, or boron. Suitable heterocycloalkyls include, for example, piperazinyl, morpholinyl, tetrahydropyranyl, tetrahydrofuranyl, piperidinyl, pyrrolidinyl, oxazolinyl and the like.

[0040] "Substituted heterocycloalkyl" refers to heterocycloalkyl as just described including in which one or more hydrogen atom to any atom of the heterocycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted heterocycloalkyl radicals include, for example, N-methylpiperazinyl, 3-dimethylaminomorpholinyl and the like.

[0041] The term "aryl" is used herein to refer to an aromatic substituent, which may be a single aromatic ring or multiple aromatic rings that are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The aromatic ring(s) may include phenyl, naphthyl, anthracenyl, and biphenyl, among others. In particular embodiments, aryls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms. In some embodiments herein, multi-ring moieties are substituents and in such an embodiment the multi-ring moiety can be attached at an appropriate atom. For example, "naphthal" can be 1-naphthyl or 2-naphthyl; "anthracenyl" can be 1-anthracenyl, 2-anthracenyl or 9-anthracenyl; and "phenanthrenyl" can be 1-phenanthrenyl, 2-phenanthrenyl, 3-phenanthrenyl, 4-phenanthrenyl or 9-phenanthrenyl.

[0042] "Substituted aryl" refers to aryl as just described in which one or more hydrogen atom bound to any carbon is replaced by one or more functional groups such as alkyl,

substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a 5 methylene or ethylene moiety. The common linking group may also be a carbonyl as in benzophenone or oxygen as in diphenylether or nitrogen in diphenylamine.

[0043] The term "heteroaryl" as used herein refers to aromatic or unsaturated rings in which one or more carbon atoms of the aromatic ring(s) are replaced by a heteroatom(s) such as nitrogen, oxygen, boron, selenium, phosphorus, silicon or sulfur. Heteroaryl 10 refers to structures that may be a single aromatic ring, multiple aromatic ring(s), or one or more aromatic rings coupled to one or more non-aromatic ring(s). In structures having multiple rings, the rings can be fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in phenyl pyridyl ketone. As used herein, rings such as thiophene, 15 pyridine, isoxazole, pyrazole, pyrrole, furan, etc. or benzo-fused analogues of these rings are defined by the term "heteroaryl."

[0044] "Substituted heteroaryl" refers to heteroaryl as just described including in which one or more hydrogen atoms bound to any atom of the heteroaryl moiety is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, 20 heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted heteroaryl radicals include, for example, 4-N,N-dimethylaminopyridine.

[0045] The term "alkoxy" is used herein to refer to the $-OZ^1$ radical, where Z^1 is selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, 25 heterocycloalkyl, substituted heterocycloalkyl, silyl groups and combinations thereof as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, benzyloxy, t-butoxy, etc. A related term is "aryloxy" where Z^1 is selected from the group consisting of aryl, substituted aryl, heteroaryl, substituted heteroaryl, and combinations thereof. Examples of suitable aryloxy radicals include phenoxy, 30 substituted phenoxy, 2-pyridinoxy, 8-quinalinoxy and the like.

[0046] As used herein the term "silyl" refers to the $-SiZ^1Z^2Z^3$ radical, where each of Z^1 , Z^2 , and Z^3 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl,

heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

[0047] As used herein the term "boryl" refers to the $-BZ^1Z^2$ group, where each of Z^1 and Z^2 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

[0048] As used herein, the term "phosphino" refers to the group $-PZ^1Z^2$, where each of Z^1 and Z^2 is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof.

[0049] As used herein, the term "phosphine" refers to the group $:PZ^1Z^2Z^3$, where each of Z^1 , Z^3 and Z^2 is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof.

[0050] The term "amino" is used herein to refer to the group $-NZ^1Z^2$, where each of Z^1 and Z^2 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0051] The term "amine" is used herein to refer to the group $:NZ^1Z^2Z^3$, where each of Z^1 , Z^2 and Z^3 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl (including pyridines), substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0052] The term "thio" is used herein to refer to the group $-SZ^1$, where Z^1 is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0053] The term "seleno" is used herein to refer to the group $-SeZ^1$, where Z^1 is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

[0054] The term "saturated" refers to lack of double and triple bonds between atoms of a

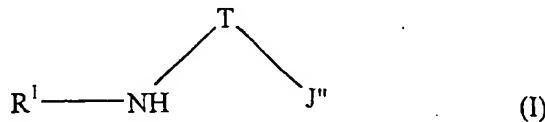
radical group such as ethyl, cyclohexyl, pyrrolidinyl, and the like.

[0055] The term "unsaturated" refers to the presence one or more double and triple bonds between atoms of a radical group such as vinyl, acetylid, oxazolinyl, cyclohexenyl, acetyl and the like.

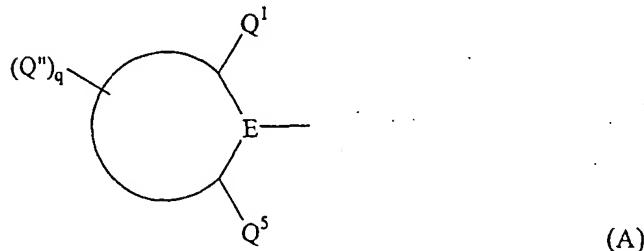
5 [0056] Other abbreviations used herein include: "Pr¹" to refer to isopropyl; "Bu¹" to refer to tertbutyl; "Me" to refer to methyl; and "Et" to refer to ethyl.

Ligands

[0057] Suitable ligands useful in this invention can be characterized broadly as 10 monoanionic ligands having an amine and a heteroaryl or substituted heteroaryl group. The ligand substituents for particular monomers are detailed near the end of this section. The ligands of the invention may be characterized by the following general formula:



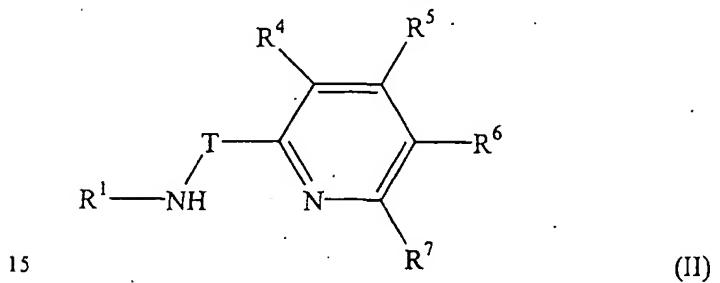
wherein R¹ is generally selected from the group consisting of alkyl, substituted alkyl, 15 cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl and combinations thereof. In many embodiments, R¹ is a ring having from 4-8 atoms in the ring generally selected from the group consisting of substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl and substituted heteroaryl, with R¹ being characterized 20 by the general formula:



where Q¹ and Q⁵ are substituents on the ring ortho to atom E, with E being selected from the group consisting of carbon and nitrogen and with at least one of Q¹ or Q⁵ being bulky (defined as having at least 2 non-hydrogen atoms). Q¹ and Q⁵ are independently selected 25 from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, aryl, substituted aryl and silyl, but provided that Q¹ and Q⁵ are not both methyl. Q''_q represents additional possible substituents on the ring, with q being 1, 2, 3, 4 or 5 and Q''

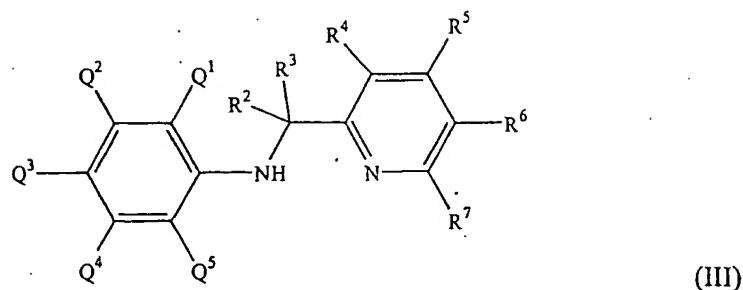
being selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. T is a bridging group selected group consisting of $-CR^2R^3-$ and $-SiR^2R^3-$ with R^2 and R^3 being independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. J" is generally selected from the group consisting of heteroaryl and substituted heteroaryl, with particular embodiments for particular reactions being described herein.

[0058] In a more specific embodiment, suitable ligands useful in this invention may be characterized by the following general formula:



wherein R^1 and T are as defined above and each of R^4 , R^5 , R^6 and R^7 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof. Optionally, any combination of R^1 , R^2 , R^3 and R^4 may be joined together in a ring structure.

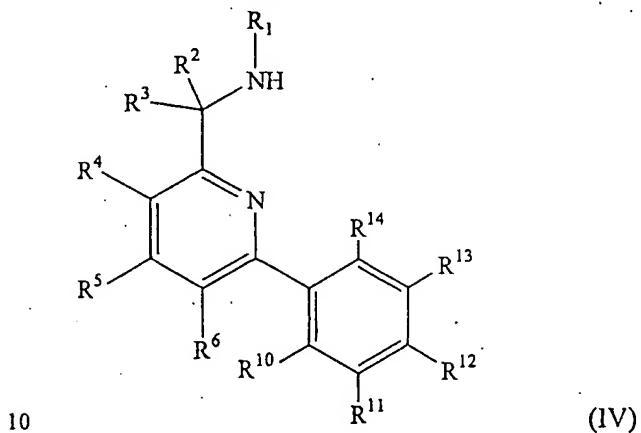
[0059] In certain more specific embodiments, the ligands in this invention may be characterized by the following general formula:



wherein Q¹, Q⁵, R², R³, R⁴, R⁵, R⁶ and R⁷ are as defined above. Q², Q³ and Q⁴ are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof.

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[0060] In other more specific embodiments, the ligands of this invention and suitable herein may be characterized by the following general formula:



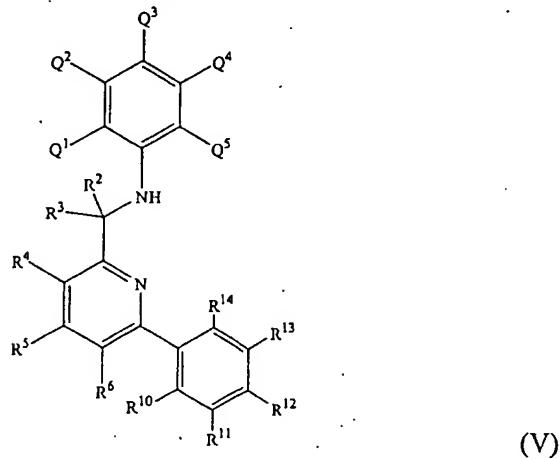
10 wherein R¹, R², R³, R⁴, R⁵, and R⁶ are as defined above. In this embodiment the R⁷ substituent has been replaced with an aryl or substituted aryl group, with R¹⁰, R¹¹, R¹² and R¹³ being independently selected from the group consisting of hydrogen, halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof; optionally, two or more R¹⁰, R¹¹, R¹² and R¹³ groups may be joined to form a fused ring system having from 3-50 non-hydrogen atoms. R¹⁴ is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl,

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substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, halide, nitro, and combinations thereof.

[0061] In still more specific embodiments, the ligands in this invention may be characterized by the general formula:



wherein R^2-R^6 , $R^{10}-R^{14}$ and Q^1-Q^5 are all as defined above.

[0062] In certain embodiments, R^2 is preferably hydrogen. Also preferably, each of R^4 and R^5 is hydrogen and R^6 is either hydrogen or is joined to R^7 to form a fused ring system. Also preferred is where R^3 is selected from the group consisting of benzyl, phenyl, naphthyl, 2-biphenyl, t-butyl, 2-dimethylaminophenyl (2-(NMe₂)-C₆H₄-), 2-methoxyphenyl (2-MeO-C₆H₄-), anthracenyl, mesityl, 2-pyridyl, 3,5-dimethylphenyl, o-tolyl and phenanthrenyl. Also preferred is where R^1 is selected from the group consisting of mesityl, 4-isopropylphenyl (4-Pr¹-C₆H₄-), napthyl, 3,5-(CF₃)₂-C₆H₃-, 2-Me-naphthyl, 2,6-(Pr¹)₂-C₆H₃-, 2-biphenyl, 2-Me-4-MeO-C₆H₃-, 2-Bu¹-C₆H₄-, 2,5-(Bu¹)₂-C₆H₃-, 2-Pr¹-6-Me-C₆H₃-, 2-Bu¹-6-Me-C₆H₃-, 2,6-Et₂-C₆H₃- or 2-sec-butyl-6-Et-C₆H₃-. Also preferred is where R^7 is selected from the group consisting of hydrogen, phenyl, napthyl, methyl, anthracenyl, phenanthrenyl, mesityl, 3,5-(CF₃)₂-C₆H₃-, 2-CF₃-C₆H₄-, 4-CF₃-C₆H₄-, 3,5-F₂-C₆H₃-, 4-F-C₆H₄-, 2,4-F₂-C₆H₃-, 4-(NMe₂)-C₆H₄-, 3-MeO-C₆H₄-, 4-MeO-C₆H₄-, 3,5-Me₂-C₆H₃-, o-tolyl, 2,6-F₂-C₆H₃- or where R^7 is joined together with R^6 to form a fused ring system, e.g., quinoline. In some preferred embodiment, R^4 , R^5 and R^6 are each independently selected from the group consisting of alkyl, aryl, halide, alkoxy, aryloxy, amino, and thio.

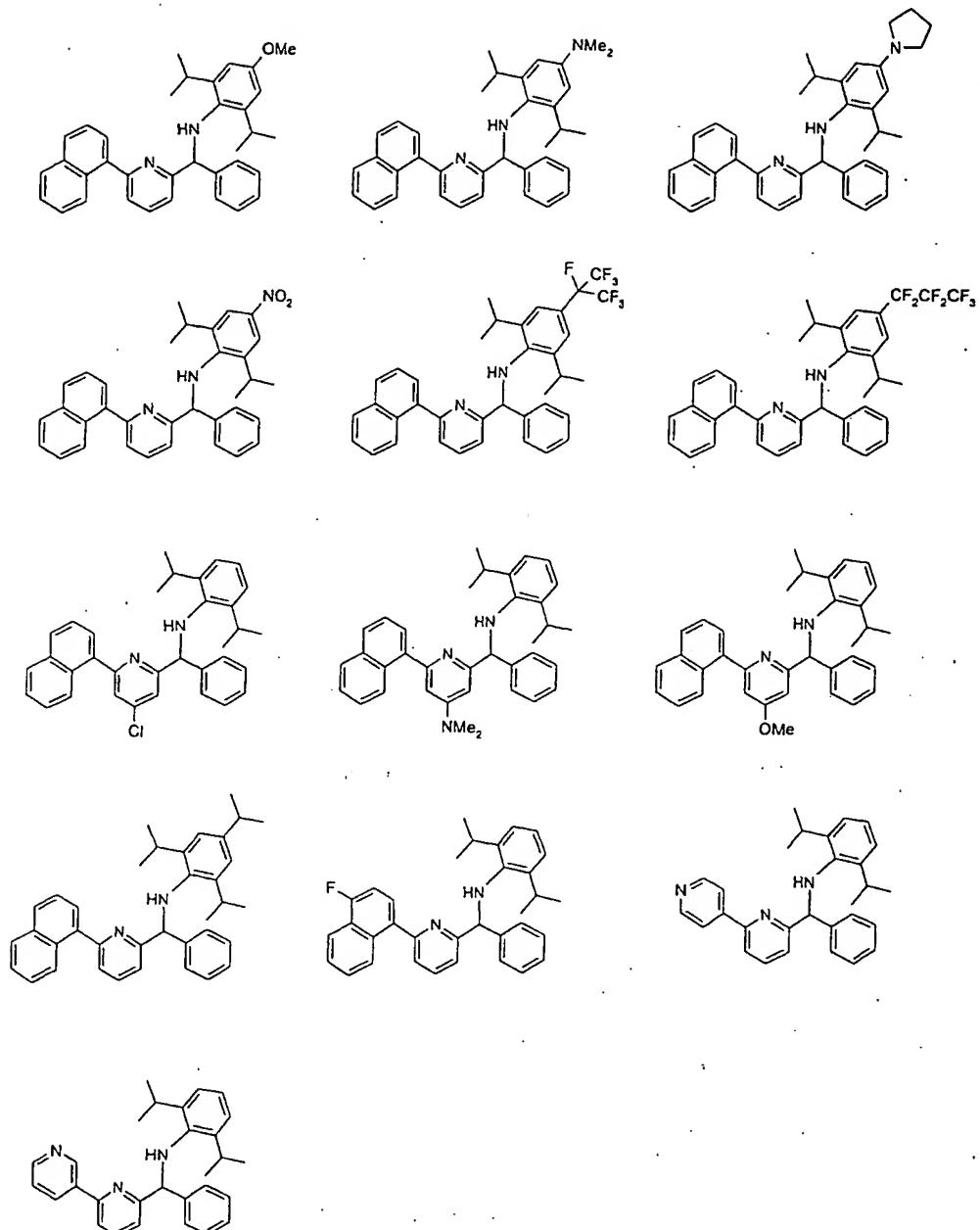
[0063] In some embodiments, Q^1 and Q^5 are, independently, selected from the group

consisting of $-\text{CH}_2\text{R}^{15}$, $-\text{CHR}^{16}\text{R}^{17}$ and methyl, provided that not both Q^1 and Q^5 are methyl. In these embodiments, R^{15} is selected from the group consisting of alkyl, substituted alkyl, aryl and substituted aryl. R^{16} and R^{17} are independently selected from the group consisting of alkyl, substituted alkyl, aryl and substituted aryl; and optionally 5 R^{16} and R^{17} are joined together in a ring structure having from 3-50 non-hydrogen atoms.

[0064] Also optionally, two or more R^4 , R^5 , R^6 , R^7 groups may be joined to form a fused ring system having from 3-50 non-hydrogen atoms in addition to the pyridine ring, e.g. generating a quinoline group. In these embodiments, R^3 is selected from the group consisting of aryl, substituted aryl, heteroaryl, substituted heteroaryl, primary and 10 secondary alkyl groups, and $-\text{PY}_2$ where Y is selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl.

[0065] Optionally within above formulas IV and V, R^6 and R^{10} may be joined to form a ring system having from 5-50 non-hydrogen atoms. For example, if R^6 and R^{10} together 15 form a methylene, the ring will have 5 atoms in the backbone of the ring, which may or may not be substituted with other atoms. Also for example, if R^6 and R^{10} together form an ethylene, the ring will have 6 atoms in the backbone of the ring, which may or may not be substituted with other atoms. Substituents from the ring can be selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, 20 substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof.

[0066] Specific examples of ligands within the scope of these formulas include:

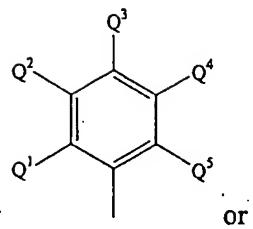


[0067] In certain embodiments, the ligands are novel compounds and those of skill in the art will be able to identify such compounds from the above. One example of the novel ligand compounds, includes those compounds generally characterized by formula (III), above where R^2 is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, aryl, and substituted aryl; and R^3 is a phosphino characterized by the formula $-PZ^1Z^2$, where each of Z^1 and Z^2 is independently selected

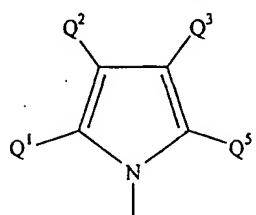
from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof. Particularly preferred embodiments of these compounds include those where Z^1 and Z^2 are each independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, aryl, and substituted aryl; and more specifically phenyl; where Q^1 , Q^3 , and Q^5 are each selected from the group consisting of alkyl and substituted alkyl and each of Q^2 and Q^4 is hydrogen; and where R^4 , R^5 , R^6 and R^7 are each hydrogen.

[0068] Certain embodiments of these ligands are preferred for the polymerization of certain monomers. In any of the above formulas I, II, III, IV or V, for the production of isotactic polypropylene it is an aspect of this invention that R^2 cannot be the same group as R^3 , leading to a chiral center on the carbon atom from which R^2 and R^3 stem. Thus, generally, R^3 may be selected from the group consisting of hydrogen, halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof, but it has also been learned that for isotactic polypropylene production R^3 is aryl, substituted aryl, heteroaryl or substituted heteroaryl. In more specific embodiments for isotactic polypropylene production R^3 is selected from the group consisting of benzyl, phenyl, naphthyl, 2-biphenyl, 2-dimethylaminophenyl, 2-methoxyphenyl, anthracenyl, mesityl, 2-pyridyl, 3,5-dimethylphenyl, o-tolyl, or phenanthrenyl. Also here, R^1 is selected from the group consisting of $2,6-(Pr^i)_2-C_6H_3-$, $2-Pr^i-6-Me-C_6H_3-$, $2,6-Et_2-C_6H_3-$ or $2-sec-butyl-6-Et-C_6H_3-$.

[0069] Also for isotactic polypropylene production it is preferred that within formula A, above, it is currently preferred that Q^1 and Q^5 are alkyl, substituted alkyl, heteroalkyl, substituted heteroalkyl, silyl, cycloalkyl, or substituted cycloalkyl, provided that Q^1 and Q^5 are not both methyl. Here also, Q^1 and Q^5 can be, independently, selected from the group consisting of $-CH_2R^{15}$, $-CHR^{16}R^{17}$ and methyl, provided that not both Q^1 and Q^5 are methyl. In a more specific embodiment for isotactic polypropylene production, it is currently preferred that Q^1 and Q^5 are both isopropyl; or both ethyl; or both sec-butyl; or Q^1 is methyl and Q^5 is isopropyl; or Q^1 is ethyl and Q^5 is sec-butyl. Even more



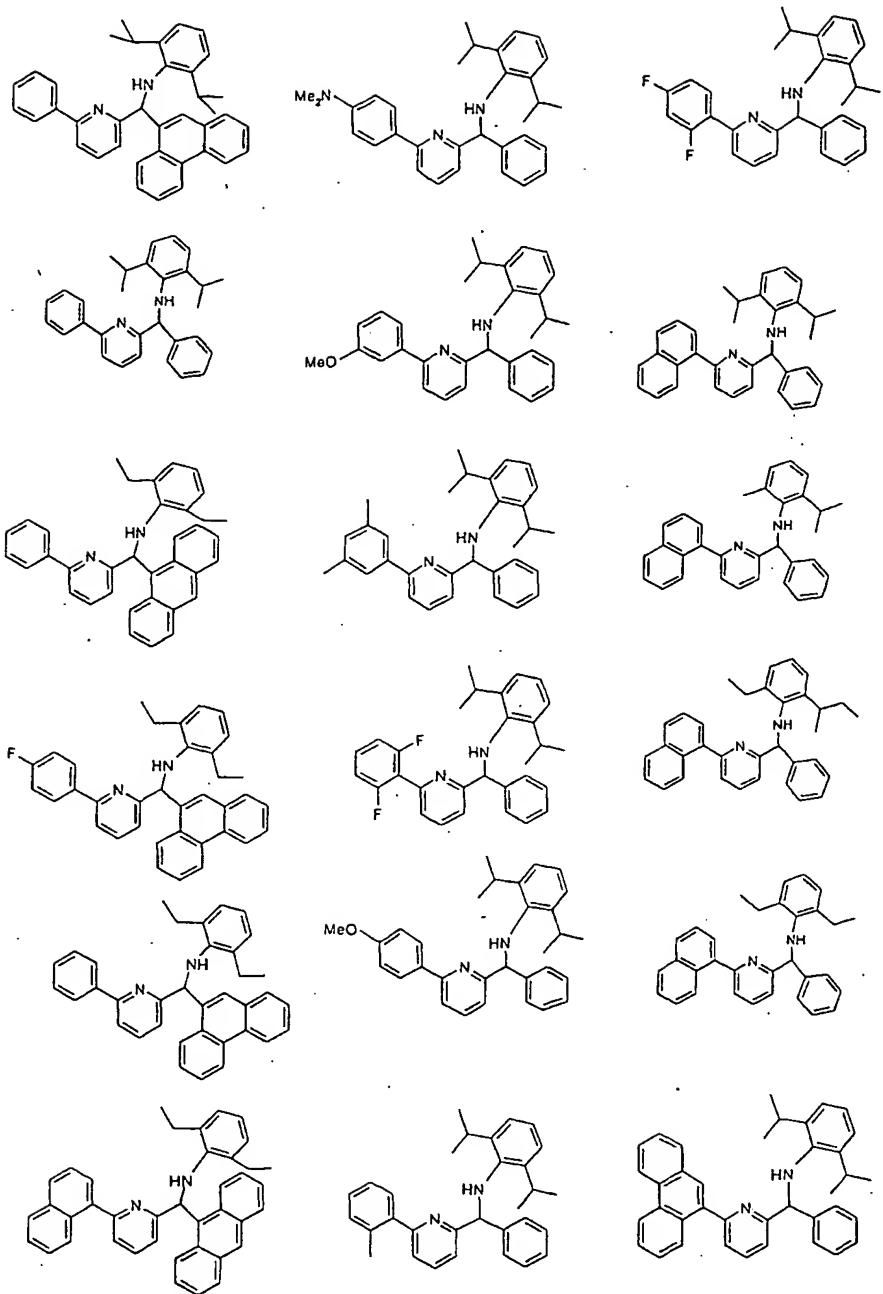
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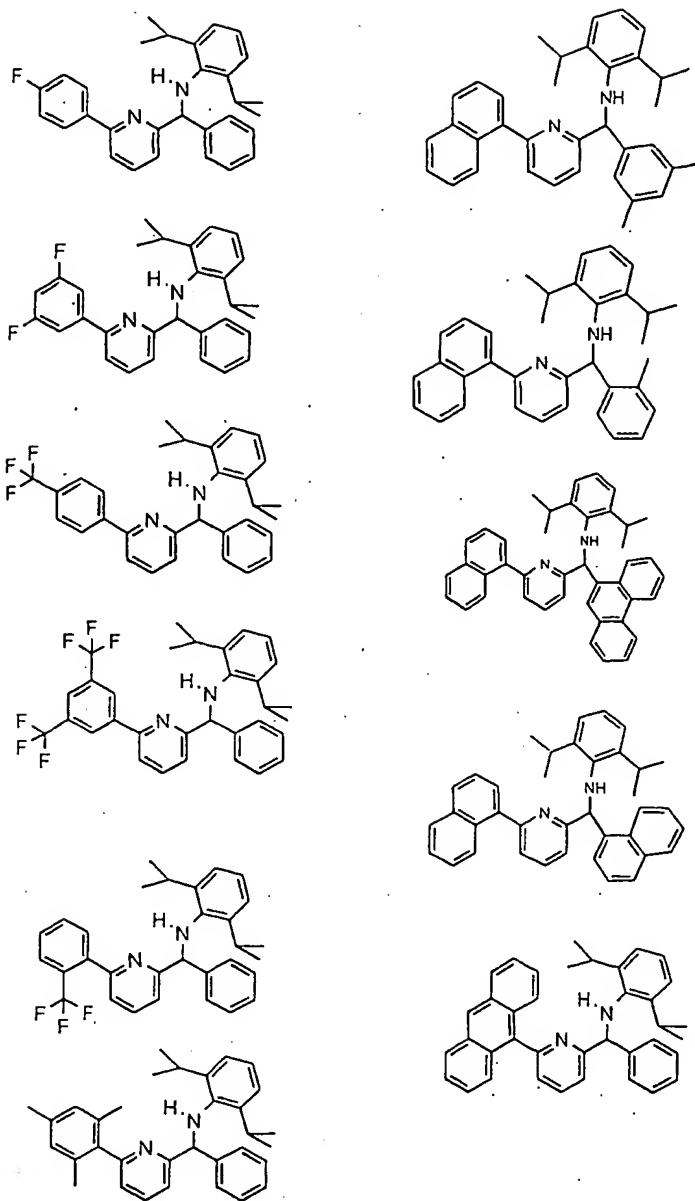


with the above definitions of the variables applying.

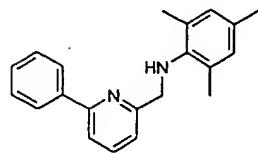
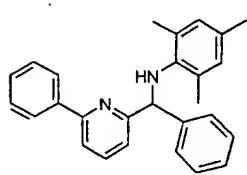
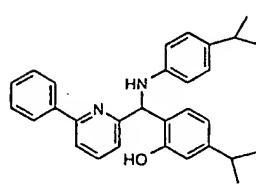
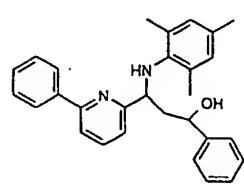
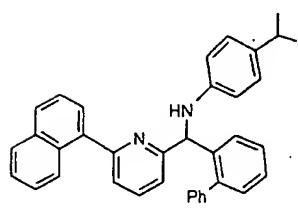
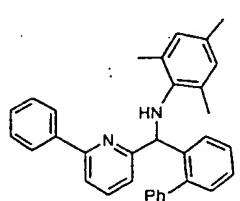
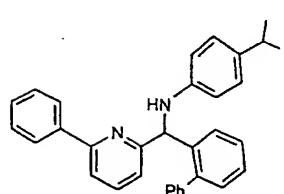
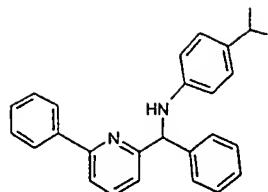
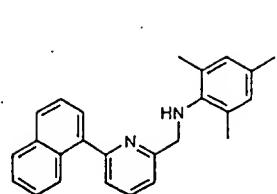
[0070] For isotactic polypropylene production it is preferred R⁷ is aryl, substituted aryl, heteroaryl or substituted heteroaryl, and more specifically R⁷ is phenyl, napthyl, mesityl, 5 anthracenyl or phenanthrenyl. Thus, most preferably, formulas IV and V above apply to isotactic polypropylene production, with it currently being preferred that R¹⁰, R¹¹, R¹², R¹³, are each hydrogen; or one or more of R¹⁰, R¹¹, R¹², R¹³ are methyl, fluoro, trifluoromethyl, methoxy, or dimethylamino; or where R¹⁰ and R¹¹ are joined to form a benzene ring and R¹² and R¹³ are each hydrogen (thus forming a napthyl group with the 10 existing phenyl ring).

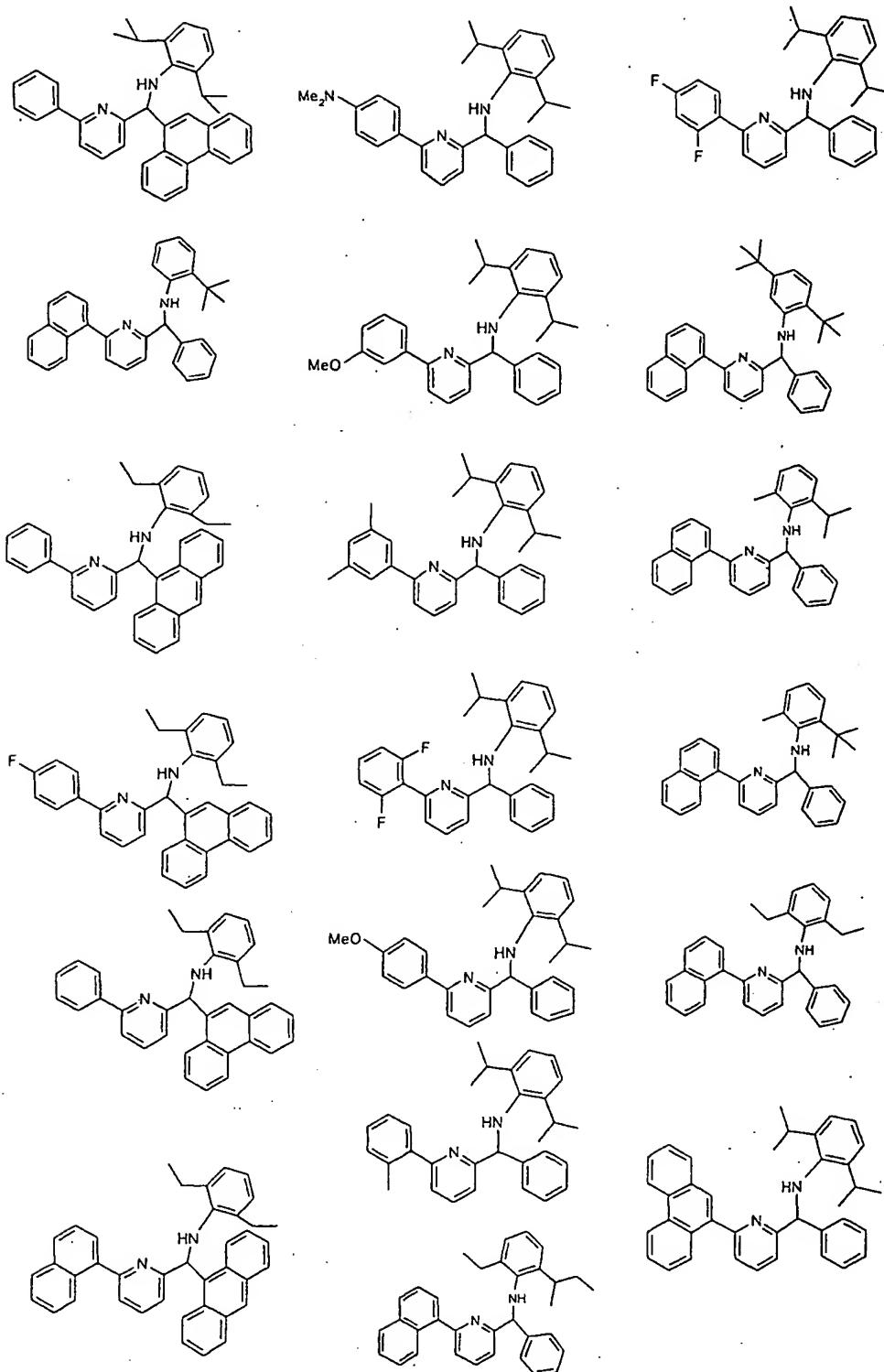
[0071] Specific ligands that are preferred for the production of crystalline polypropylene are:

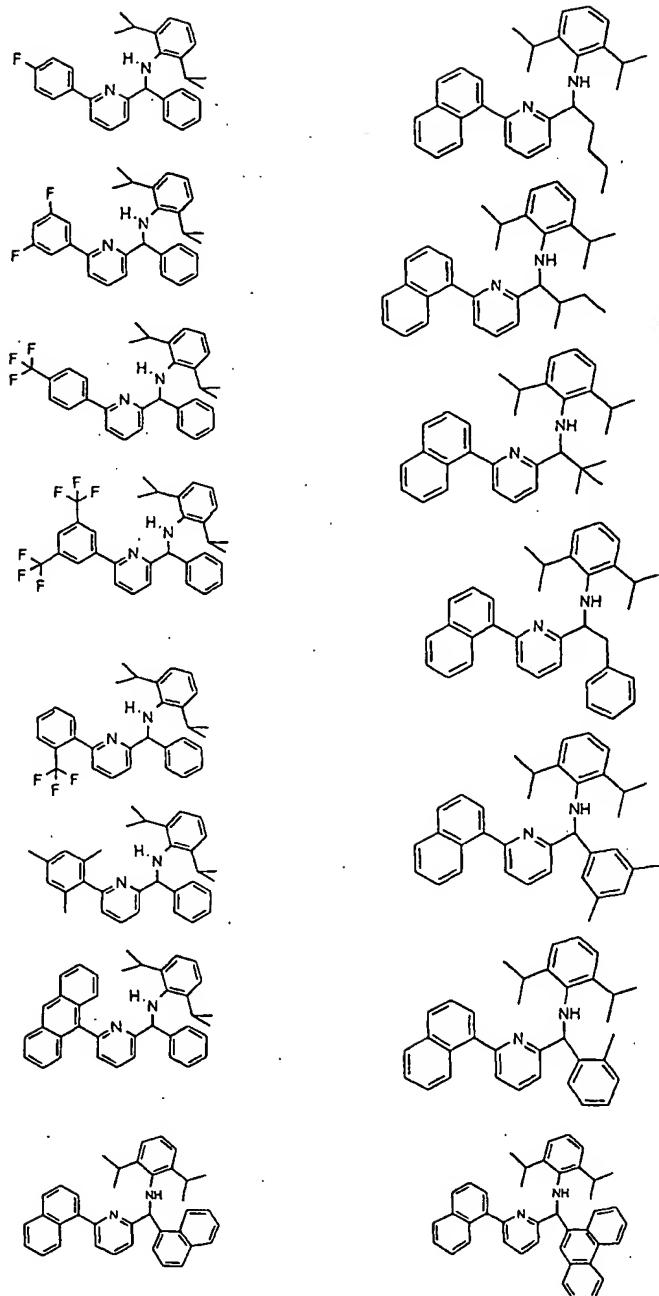


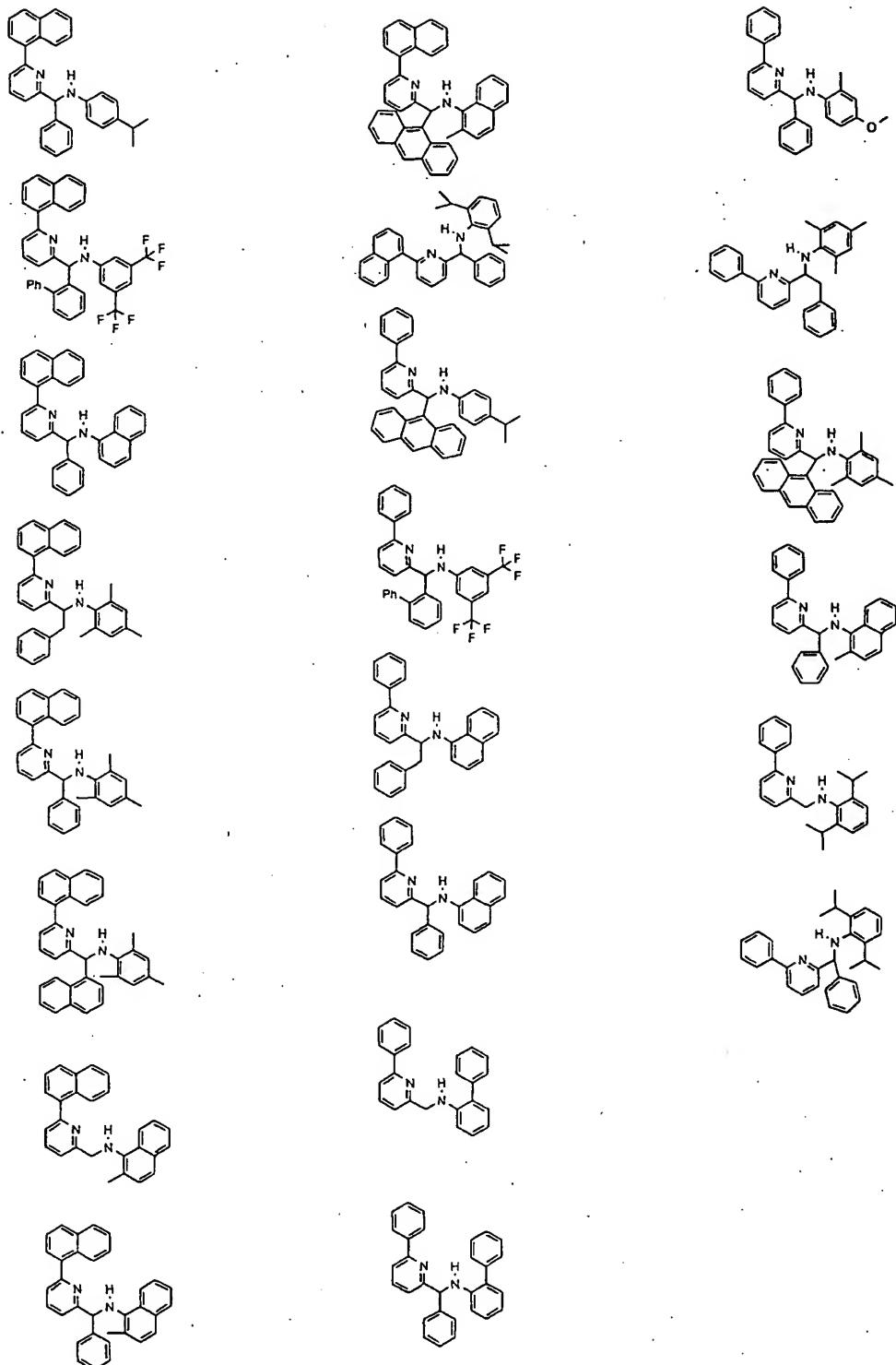


[0072] For the production of ethylene-styrene copolymers, there are different preferences depending on the type of polymer that is desired. In some embodiments, it is preferred that the ligands of either of formulas II, III, IV or V is used, particularly with R⁷ selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl. 5 Specific ligands that are preferred for ethylene-styrene copolymer production are:



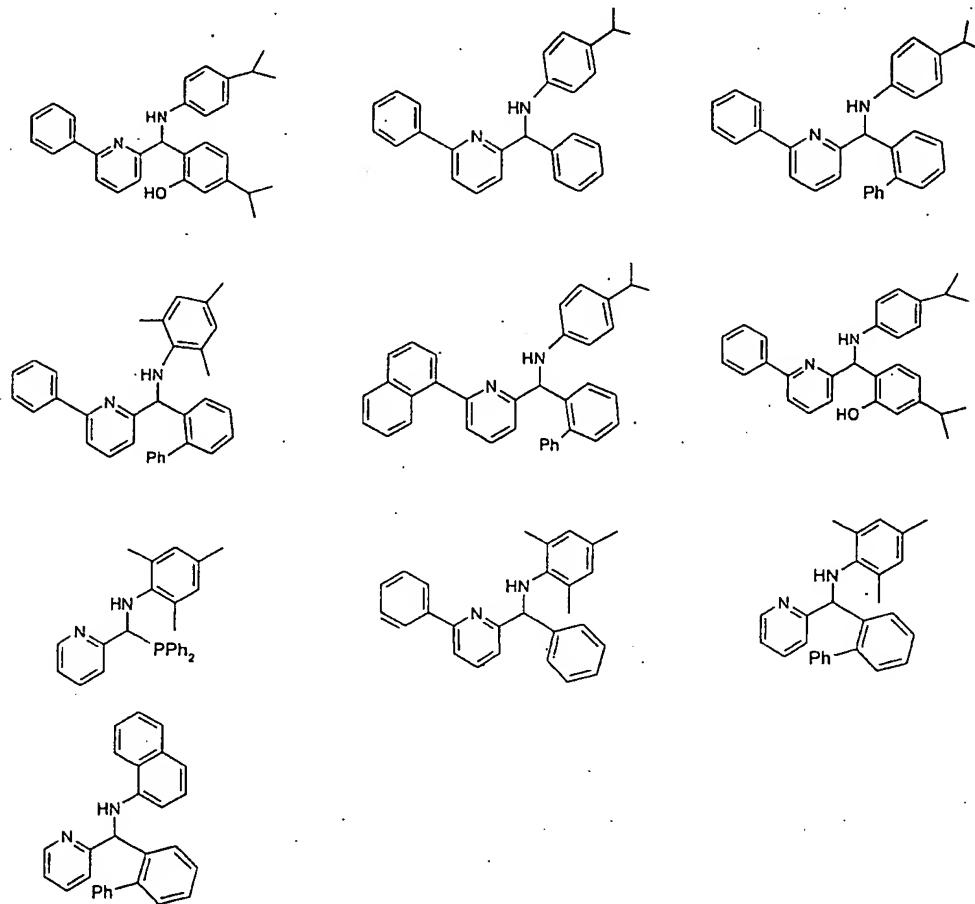


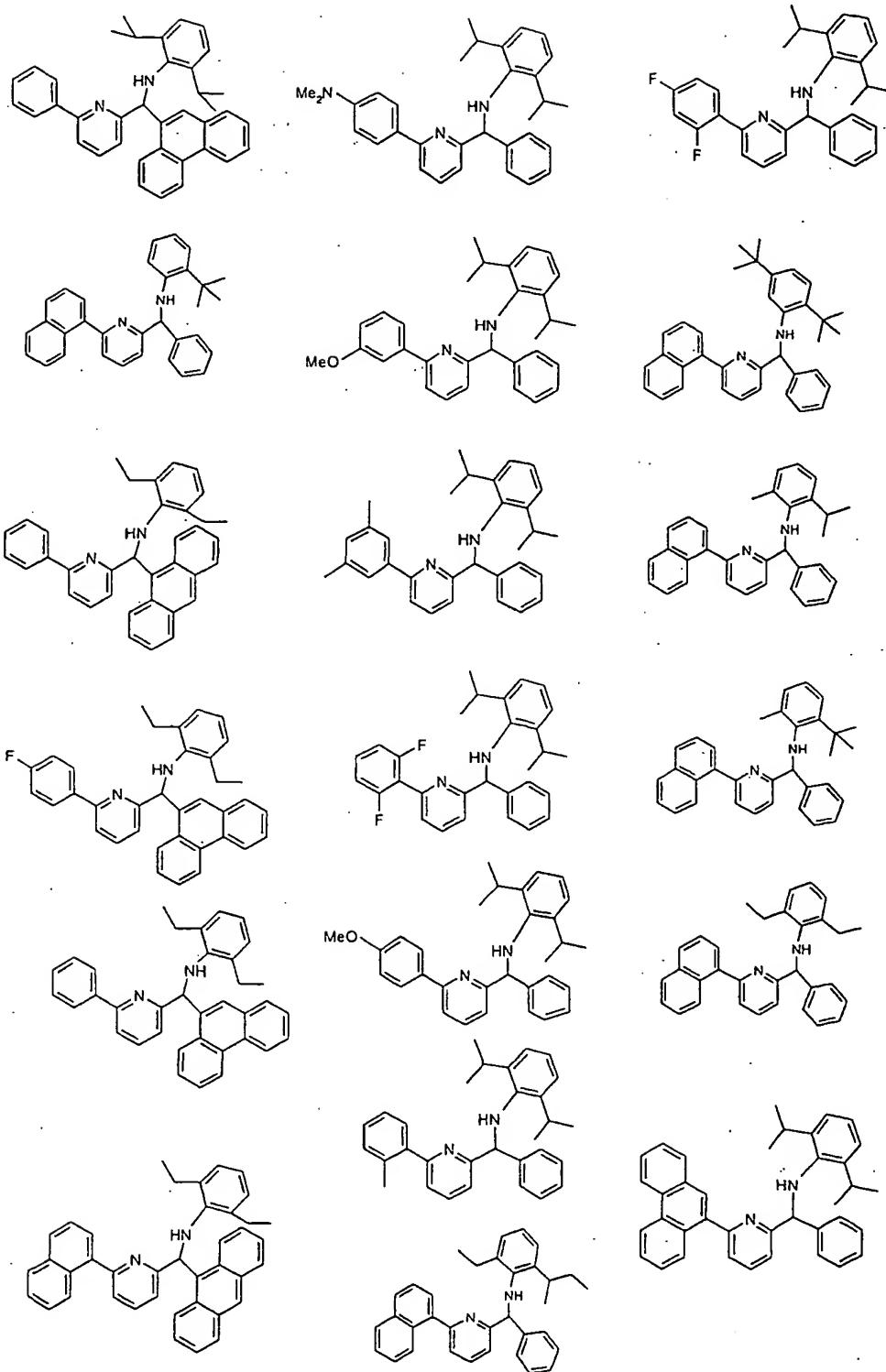


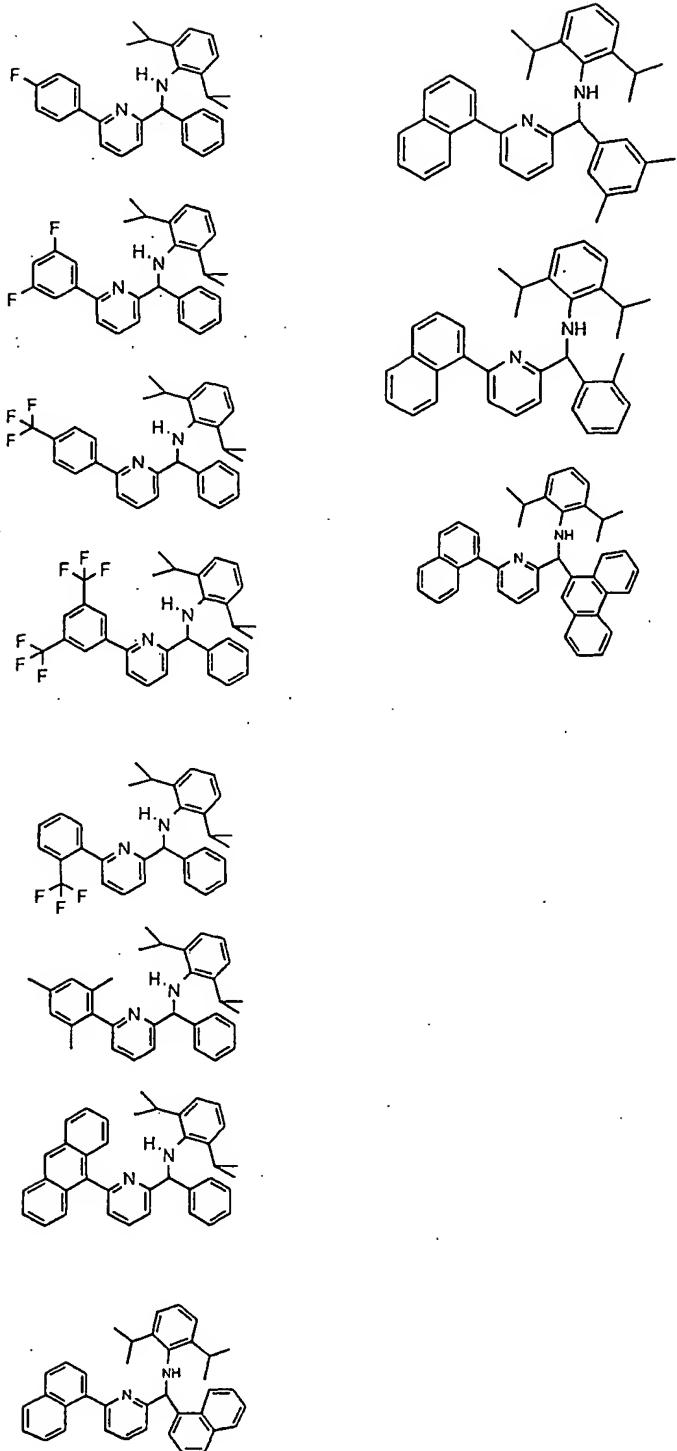


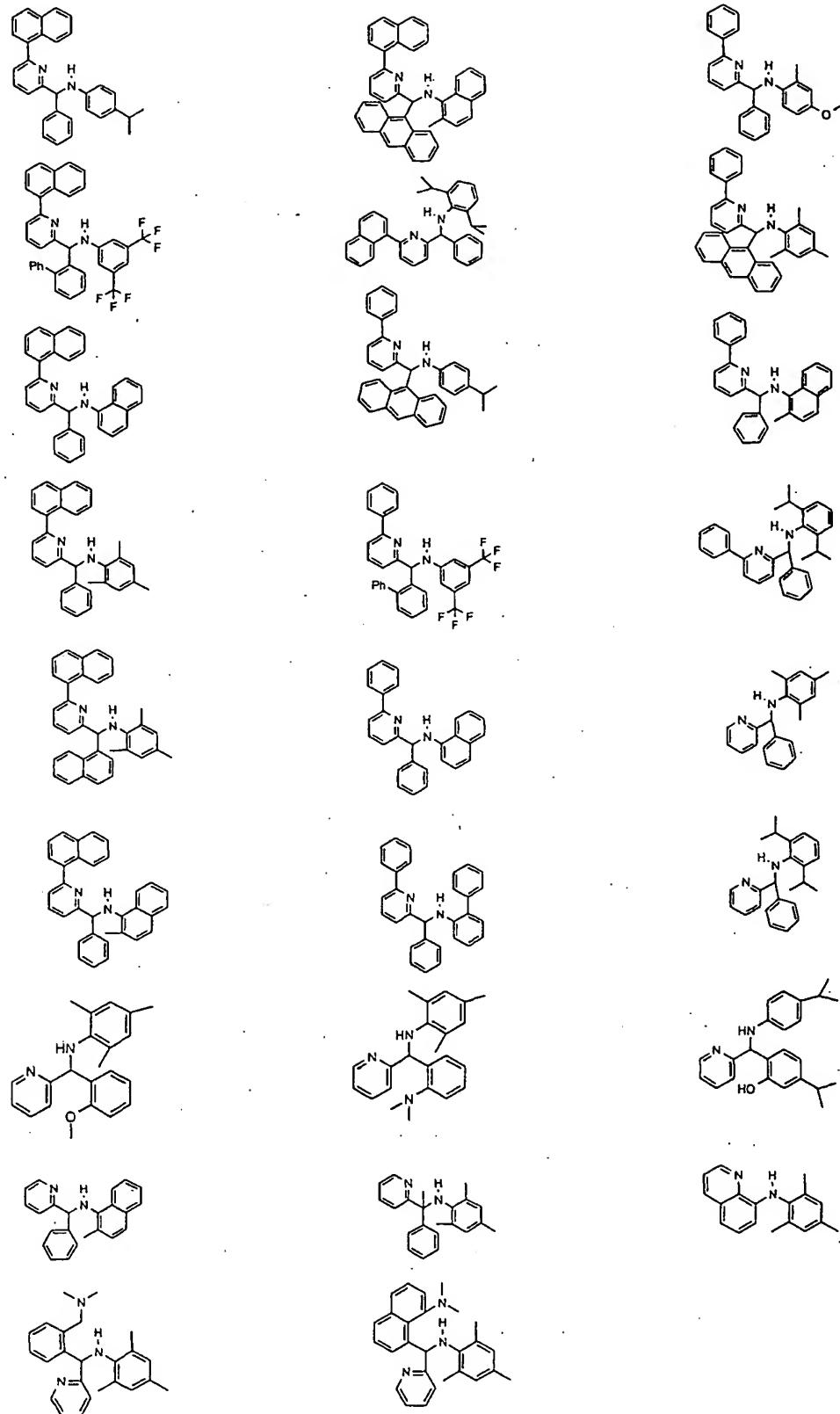
[0073] For the production of ethylene-1-octene copolymers, it is preferred that the ligands of either of formulas II, III, IV or V is used, with either or both of R^3 and/or R^7

being independently selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Specific ligands that are preferred for ethylene-1-octene copolymer production are:

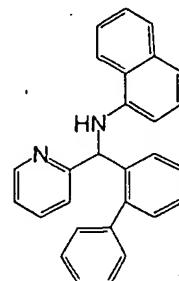
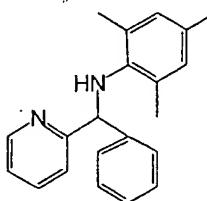
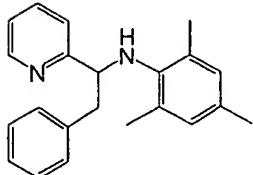
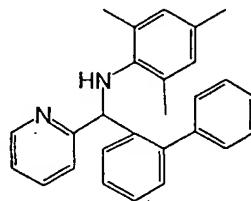
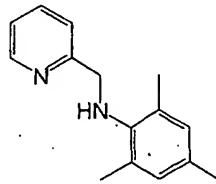
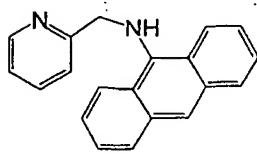




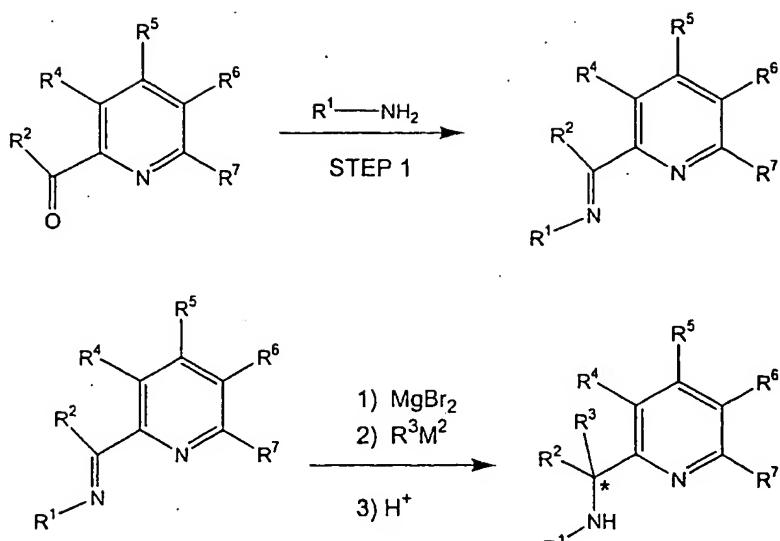




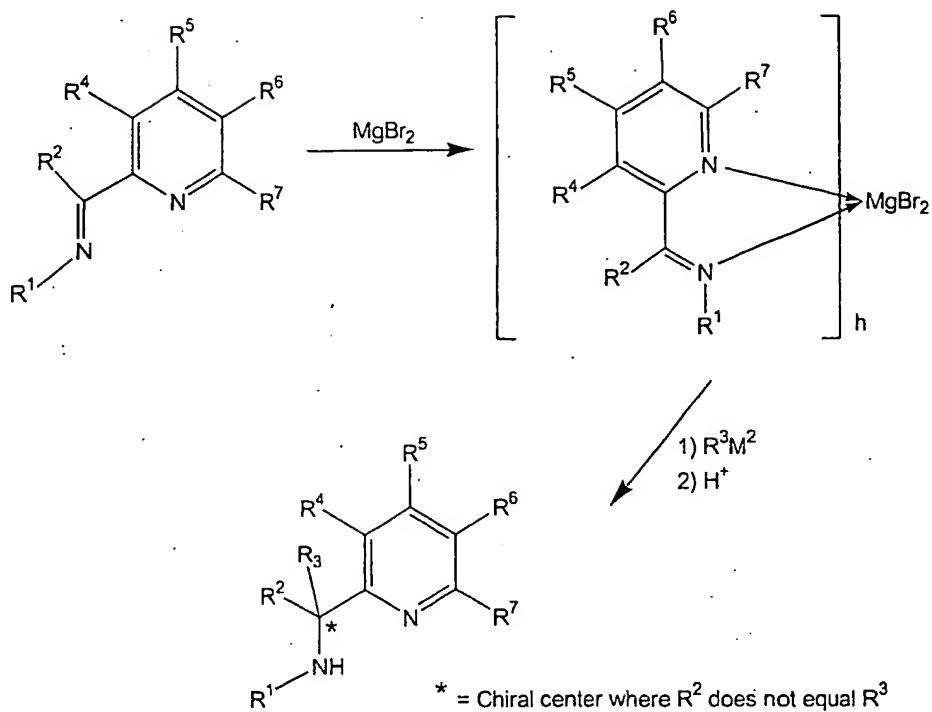
[0074] For the production of ethylene-isobutylene copolymers, it is currently preferred that R² and R³ are either both hydrogen or R² is hydrogen and R³ is aryl, substituted aryl or substituted alkyl. It is also important for ethylene-isobutylene copolymerization that R⁷ is hydrogen. Specific ligands useful in this invention for the production of ethylene-isobutylene copolymers include:



[0075] The ligands of the invention may be prepared using known procedures. See, for example, Advanced Organic Chemistry, March, Wiley, New York 1992 (4th Ed.). Specifically, the ligands of the invention may be prepared using the two step procedure outlined in Scheme 1.



[0076] In Scheme 1, the * represents a chiral center when R^2 and R^3 are not identical; 5 also, the R groups have the same definitions as above. Generally, R^3M^2 is a nucleophile such as an alkylating or arylating or hydrogenating reagent and M^2 is a metal such as a main group metal, or a metalloid such as boron. The alkylating, arylating or hydrogenating reagent may be a Grignard, alkyl, aryl-lithium or borohydride reagent. Scheme 1, step 2 first employs the use of complexing reagent. Preferably, as in the case 10 of Scheme 1, magnesium bromide is used as the complexing reagent. The role of the complexing reagent is to direct the nucleophile, R^3M^2 , selectively to the imine carbon. Where the presence of functional groups impede this synthetic approach, alternative synthetic strategies may be employed. For instance, ligands where R^3 = phosphino can be prepared in accordance with the teachings of U.S. 6,034,240 and U.S. 6,043,363. In 15 addition, tetra-alkylhafnium compounds or tetra-substituted alkylhafnium compounds or tetra-arylhafnium compounds or tetra-substituted arylhafnium compounds may be employed in step 2, in accordance with the teachings of U.S. 6,103,657, which is incorporated herein by reference. Scheme 2 further describes a synthesis process:



Scheme 2

[0077] In scheme 2, $h = 1$ or 2 and the bromine ions may or may not be bound to the magnesium. The effect of the complexation is to guide the subsequent nucleophilic attack by R^3M^2 to the imine carbon. Thus complexation may lead to a more selective reaction that may increase the yield of the desired ancillary ligands. Using this technique, selectivity is generally greater than about 50%, more preferably greater than about 70% and even more preferably greater than about 80%. Complexation may be particularly useful for the preparation of arrays of ancillary ligands of the type disclosed in the invention, where R^3 is a variable in the preparation of the ancillary ligand array. As shown in Scheme 2 by the *, where R^2 and R^3 are different, this approach also leads to the formation of a chiral center on the ancillary ligands of the invention. Under some circumstances R^3M^2 may be successfully added to the imine in the absence the complexing reagent. Ancillary ligands that possess chirality may be important in certain olefin polymerization reactions, particularly those that lead to a stereospecific polymer, see "Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts", Brintzinger, et al., *Angew. Chem. Int. Ed. Engl.*, 1995, Vol. 34, pp. 1143-1170, and the references therein; Bercaw et al., *J. Am. Chem. Soc.*, 1999, Vol. 121, 564-573; and Bercaw et al., *J. Am. Chem. Soc.*, 1996, Vol. 118, 11988-11989; each of which is

incorporated herein by reference.

[0078] In the practice of high throughput methods or combinatorial materials science, introduction of diversity may be important in designing libraries or arrays. The synthetic schemes discussed herein will allow those of skill in the art to introduce diversity on the 5 ligands, which may assist in optimizing the selection of a particular ligand for a particular polymerization reaction. Step 1 (see Scheme1) may be conducted with, for example, any combination of the pyridines and anilines shown in Tables 1 and 2 (shown in Figures 1 and 2, respectively). The compounds shown in Tables 1 and 2 are meant to be illustrative and non-limiting.

10

Compositions

[0079] Once the desired ligand is formed, it may be combined with a metal atom, ion, compound or other metal precursor compound. In some applications, the ligands of this invention will be combined with a metal compound or precursor and the product of such 15 combination is not determined, if a product forms. For example, the ligand may be added to a reaction vessel at the same time as the metal or metal precursor compound along with the reactants, activators, scavengers, etc. Additionally, the ligand can be modified prior to addition to or after the addition of the metal precursor, e.g. through a deprotonation reaction or some other modification.

20 [0080] For formulas I, II, III, IV and V, the metal precursor compounds may be characterized by the general formula $Hf(L)_n$ where L is independently selected from the group consisting of halide (F, Cl, Br, I), alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and optionally two or more L groups may be linked together in a ring structure. n is 1, 2, 3, 4, 5, or 6. The hafnium precursors may be 25 monomeric, dimeric or higher orders thereof. It is well known that hafnium metal aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and optionally two or more L groups may be linked together in a ring structure. n is 1, 2, 3, 4, 5, or 6. The hafnium precursors may be monomeric, dimeric or higher orders thereof. It is well known that hafnium metal typically contains some amount of impurity of zirconium. Thus, this invention uses as 30 pure hafnium as is commercially reasonable. Specific examples of suitable hafnium precursors include, but are not limited to $HfCl_4$, $Hf(CH_2Ph)_4$, $Hf(CH_2CMe_3)_4$, $Hf(CH_2SiMe_3)_4$, $Hf(CH_2Ph)_3Cl$, $Hf(CH_2CMe_3)_3Cl$, $Hf(CH_2SiMe_3)_3Cl$, $Hf(CH_2Ph)_2Cl_2$,

Hf(CH₂CMe₃)₂Cl₂, Hf(CH₂SiMe₃)₂Cl₂, Hf(NMe₂)₄, Hf(NEt₂)₄, and Hf(N(SiMe₃)₂)₂Cl₂.

Lewis base adducts of these examples are also suitable as hafnium precursors, for example, ethers, amines, thioethers, phosphines and the like are suitable as Lewis bases.

Specific examples include HfCl₄(THF)₂, HfCl₄(SMe₂)₂ and Hf(CH₂Ph)₂Cl₂(OEt₂).

5 [0081] For formulas IV and V, the metal precursor compounds may be characterized by the general formula M(L)_n where M is hafnium or zirconium and each L is independently selected from the group consisting of halide (F, Cl, Br, I), alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, 10 alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof. Optionally two or more L groups may be linked together in a ring structure. n is 4, typically. It is well known that hafnium metal typically contains some amount of impurity of zirconium. Thus, this 15 invention uses as pure hafnium or zirconium as is commercially reasonable. Specific examples of suitable hafnium and zirconium precursors include, but are not limited to HfCl₄, Hf(CH₂Ph)₄, Hf(CH₂CMe₃)₄, Hf(CH₂SiMe₃)₄, Hf(CH₂Ph)₃Cl, Hf(CH₂CMe₃)₃Cl, Hf(CH₂SiMe₃)₃Cl, Hf(CH₂Ph)₂Cl₂, Hf(CH₂CMe₃)₂Cl₂, Hf(CH₂SiMe₃)₂Cl₂, Hf(NMe₂)₄, Hf(NEt₂)₄, and Hf(N(SiMe₃)₂)₂Cl₂; ZrCl₄, Zr(CH₂Ph)₄, Zr(CH₂CMe₃)₄, Zr(CH₂SiMe₃)₄, 20 Zr(CH₂Ph)₃Cl, Zr(CH₂CMe₃)₃Cl, Zr(CH₂SiMe₃)₃Cl, Zr(CH₂Ph)₂Cl₂, Zr(CH₂CMe₃)₂Cl₂, Zr(CH₂SiMe₃)₂Cl₂, Zr(NMe₂)₄, Zr(NEt₂)₄, Zr(NMe₂)₂Cl₂, Zr(NEt₂)₂Cl₂, and Zr(N(SiMe₃)₂)₂Cl₂. Lewis base adducts of these examples are also suitable as hafnium precursors, for example, ethers, amines, thioethers, phosphines and the like are suitable as Lewis bases. Specific examples include HfCl₄(THF)₂, HfCl₄(SMe₂)₂ and 25 Hf(CH₂Ph)₂Cl₂(OEt₂).

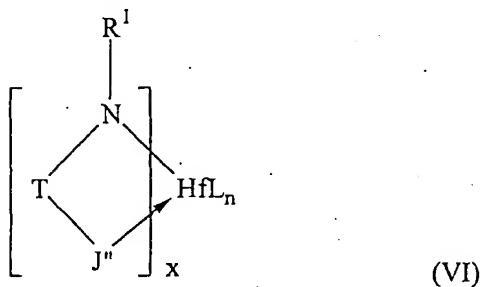
[0082] The ligand to metal precursor compound ratio is typically in the range of about 0.01:1 to about 100:1, more preferably in the range of about 0.1:1 to about 10:1.

Metal-Ligand Complexes

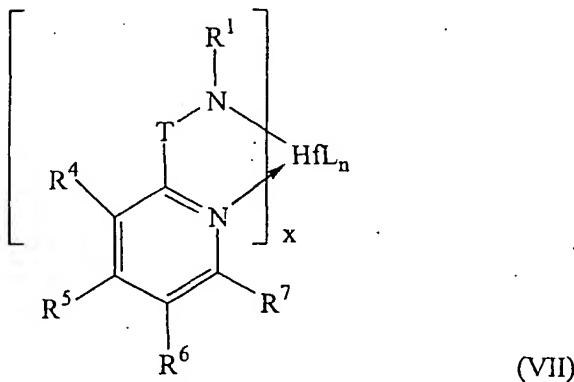
30 [0083] This invention, in part, relates to new metal-ligand complexes. Generally, the ligand is mixed with a suitable metal precursor compound prior to or simultaneously with allowing the mixture to be contacted with the reactants (e.g., monomers). When the ligand is mixed with the metal precursor compound, a metal-ligand complex may be

formed, which may be a catalyst or may need to be activated to be a catalyst. The metal-ligand complexes discussed herein are referred to as 2,1 complexes or 3,2 complexes, with the first number representing the number of coordinating atoms and second number representing the number of anionic sites on the ligand. The 2,1 complexes therefore 5 have two coordinating atoms and a single anionic charge. Other embodiments of this invention are those complexes that have a general 3,2 coordination scheme to a metal center, with 3,2 referring to a ligand that occupies three coordination sites on the metal and two of those sites being anionic and the remaining site being a neutral Lewis base type coordination.

10 [0084] Looking first at the 2,1 metal-ligand complexes, the metal-ligand complexes may be characterized by the following general formula:



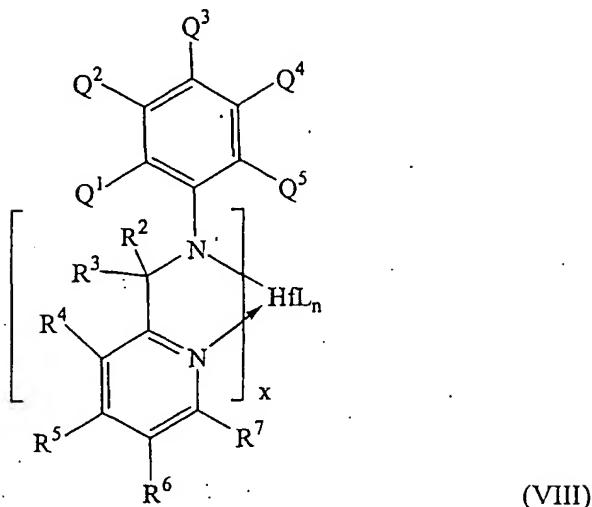
wherein T, J'', R¹, L and n are as defined previously; and x is 1 or 2. The J'' heteroaryl may or may not datively bond, but is drawn as bonding. More specifically, the metal-ligand complexes may be characterized by the formula: 15



wherein R¹, T, R⁴, R⁵, R⁶, R⁷, L and n are as defined previously; and x is 1 or 2. In one preferred embodiment x = 1 and n = 3. Additionally, Lewis base adducts of these metal-ligand complexes are also within the scope of the invention, for example, ethers, amines, 20 thioethers, phosphines and the like are suitable as Lewis bases.

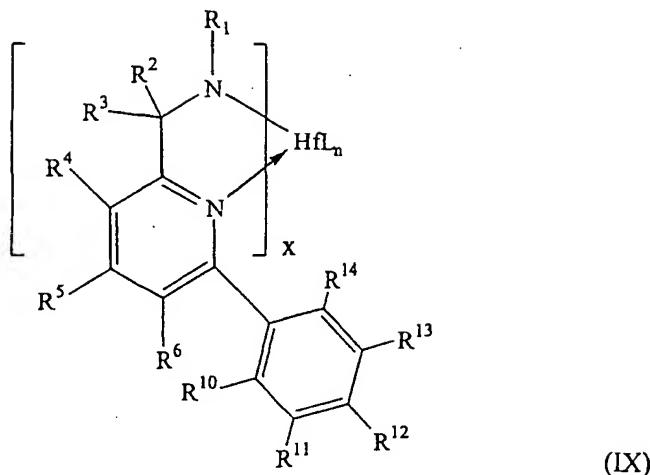
[0085] More specifically, the metal-ligand complexes of this invention may be

characterized by the general formula:



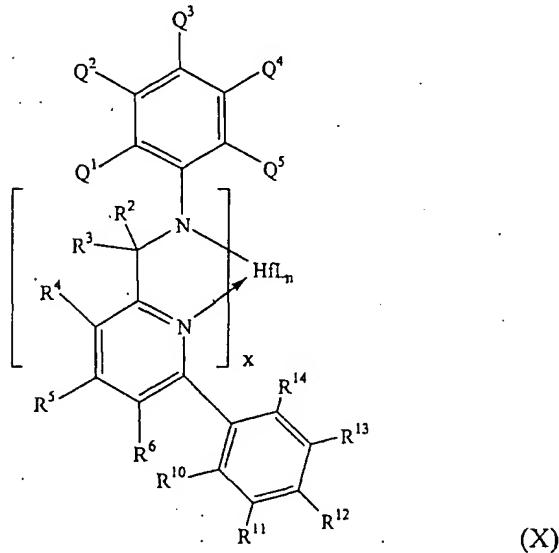
wherein the variables are generally defined above. Thus, e.g., Q², Q³, Q⁴, R², R³, R⁴, R⁵, R⁶ and R⁷ are independently selected from the group consisting of hydrogen, alkyl, 5 substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof; optionally, two or more R⁴, R⁵, R⁶, R⁷ groups may be joined to form a fused ring system having from 3-50 non-hydrogen atoms in addition to 10 the pyridine ring, e.g. generating a quinoline group; also, optionally, any combination of R², R³ and R⁴ may be joined together in a ring structure; Q¹ and Q⁵ are selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, aryl, substituted aryl, provided that Q¹ and Q⁵ are not both methyl; and each L is 15 independently selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido, allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates, carbonates, nitrates, sulphates, ethers, thioethers and combinations thereof; and optionally two L groups may 20 be linked together in a ring structure; n is 1, 2, 3, 4, 5, or 6; and x = 1 or 2.

[0086] In other embodiments, the 2,1 metal-ligand complexes can be characterized by the general formula:



wherein the variables are generally defined above.

[0087] In still other embodiments, the 2,1 metal-ligand complexes of this invention can be characterized by the general formula:

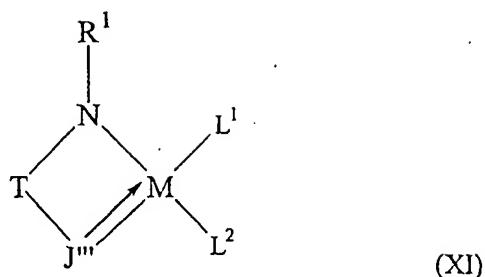


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wherein the variables are generally defined above. The more specific embodiments of the metal-ligand complexes of formulas VI, VII, VIII, IX and X are explained above with regard to the specifics described for the ligands and metal precursors.

[0088] Lewis base adducts of these complexes are also suitable, for example, ethers, 10 amines, thioethers, phosphines and the like are suitable as Lewis bases (note the definition of L).

[0089] Turning to the 3,2 metal-ligand complexes of this invention, the metal-ligand complexes in this aspect of this invention may be generally characterized by the general formula:



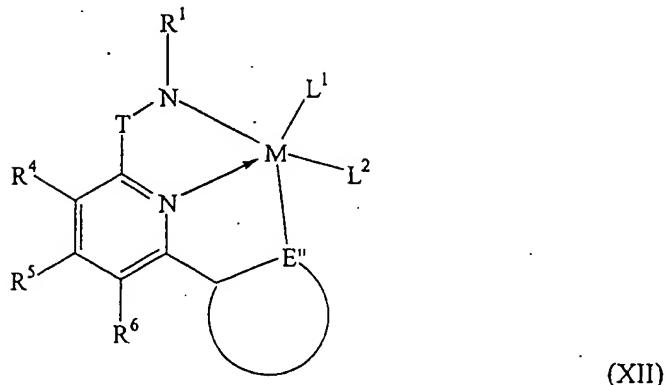
where M is zirconium or hafnium;

R¹ and T are defined above;

J''' being selected from the group of substituted heteroaryls with 2 atoms bonded

5 to the metal M, at least one of those 2 atoms being a heteroatom, and with one atom of
 J''' is bonded to M via a dative bond, the other through a covalent bond; and
 L¹ and L² are independently selected from the group consisting of halide, alkyl,
 substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl,
 heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl,
 10 substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, amino, amine, hydrido,
 allyl, diene, seleno, phosphino, phosphine, carboxylates, thio, 1,3-dionates, oxalates,
 carbonates, nitrates, sulphates, and combinations thereof; and optionally the L groups
 may be linked together in a ring structure.

[0090] More specifically, the 3,2 metal-ligand complexes of this invention may be
 15 characterized by the general formula:



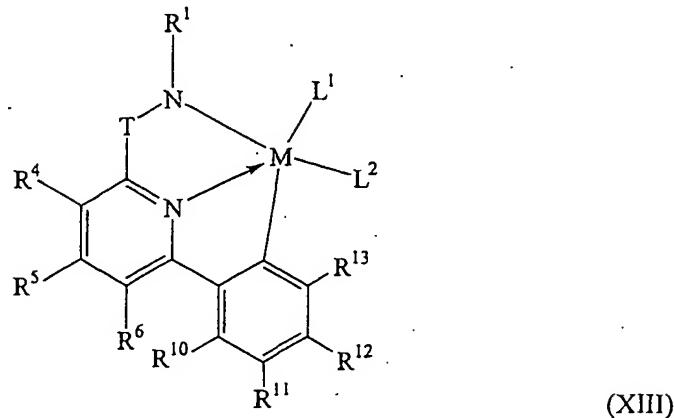
where M is zirconium or hafnium;

T, R¹, R⁴, R⁵, R⁶, L¹ and L² are defined above; and

E'' is either carbon or nitrogen and is part of an cyclic aryl, substituted aryl,
 20 heteroaryl, or substituted heteroaryl group.

[0091] Even more specifically, the 3,2 metal-ligand complexes of this invention may be

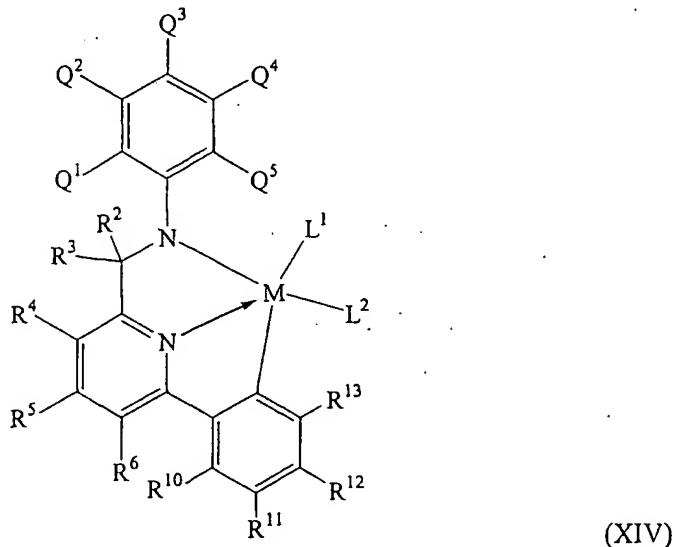
characterized by the general formula:



where M is zirconium or hafnium; and

T, R¹, R⁴, R⁵, R⁶, R¹⁰, R¹¹, R¹², R¹³, L¹ and L² are defined above.

5 [0092] Still even more specifically, the 3,2 metal-ligand complexes of this invention may be characterized by the general formula:



where M is zirconium or hafnium; and

T, R¹, R⁴, R⁵, R⁶, R¹⁰, R¹¹, R¹², R¹³, Q¹, Q², Q³, Q⁴, Q⁵, L¹ and L² are defined

10 above.

[0093] The more specific embodiments of the metal-ligand complexes of formulas XI, XII, XIII and XIV are explained above with regard to the specifics described for the ligands and metal precursors. Lewis base adducts of these complexes are also suitable, for example, ethers, amines, thioethers, phosphines and the like are suitable as Lewis bases.

[0094] In addition, preferences for the substituents on the ligands for production of the particular polymers discussed above (e.g., isotactic polypropylene) apply to the metal-ligand complexes just described. For isotactic polypropylene it is currently preferred that M is hafnium, although this preference is only slight as compared to zirconium. By 5 "slight" here, it is meant that zirconium metal based polymerization of propylene for isotactic polypropylene shows similar tacticity control as compared to hafnium metal based polymerization, however, the hafnium based catalysts tend to show better polymerization activity and performance overall.

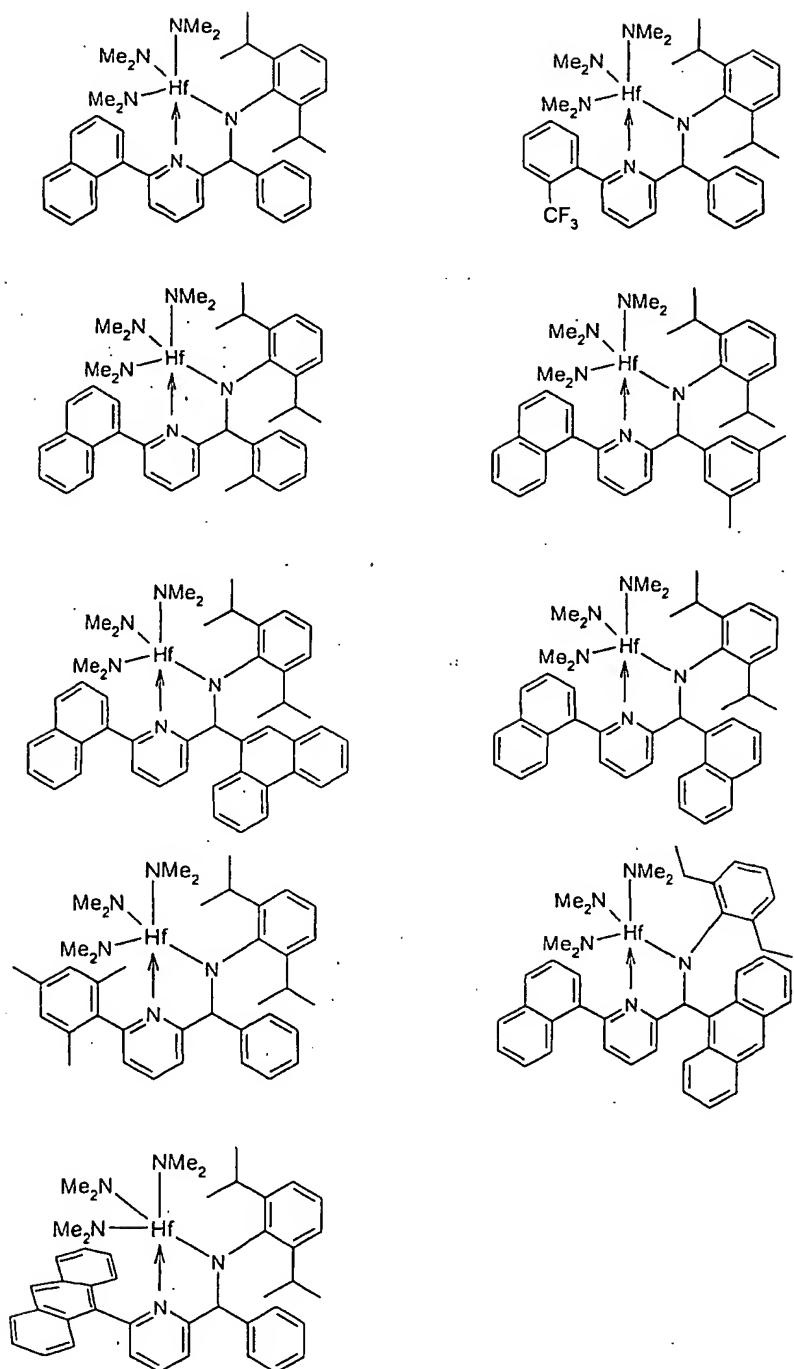
[0095] For isotactic polypropylene production, it is currently preferred that L¹ and L² are 10 the same and selected from the group consisting of alkyl and dialkyl amino, more specifically from the group consisting of methyl and dimethylamino.

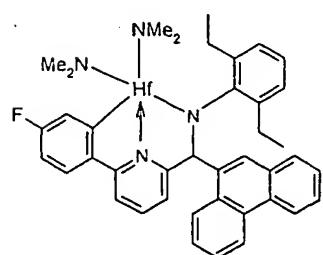
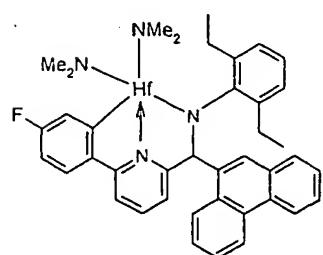
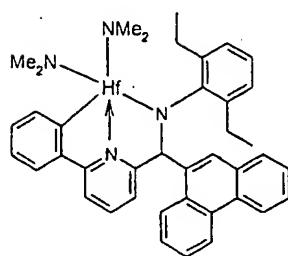
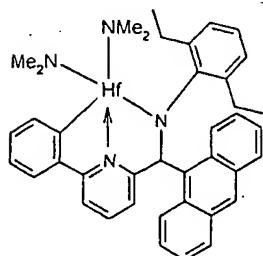
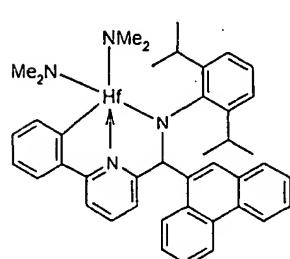
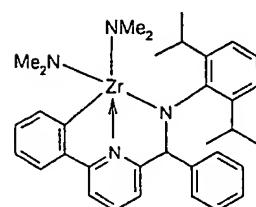
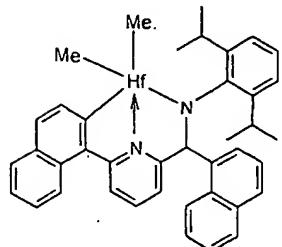
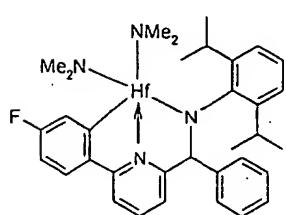
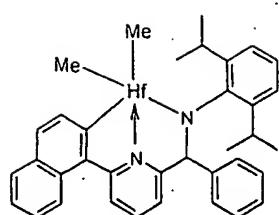
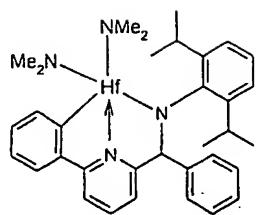
[0096] As above, for production of isotactic polypropylene, R² and R³ are not the same group, leading to a chiral center on the carbon atom from which R² and R³ stem. In more 15 specific embodiments, R² is hydrogen. In more specific embodiments for isotactic polypropylene production R³ is selected from the group consisting of hydrogen, halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof. In more specific embodiments for isotactic 20 polypropylene production R³ is aryl, substituted aryl, heteroaryl or substituted heteroaryl. In more specific embodiments for isotactic polypropylene production R³ is selected from the group consisting of benzyl, phenyl, 2-biphenyl, 2-dimethylaminophenyl, 2-methoxyphenyl, anthracenyl, mesityl, 2-pyridyl, 3,5-dimethylphenyl, o-tolyl and phenanthrenyl.

[0097] In the above formulas, R¹⁰, R¹¹, R¹² and R¹³ are independently selected from the 25 group consisting of hydrogen, halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, nitro, and combinations thereof; optionally, 30 two or more R¹⁰, R¹¹, R¹² and R¹³ groups may be joined to form a fused ring system having from 3-50 non-hydrogen atoms. Particular embodiments include, for example, for isotactic polypropylene production, it is currently preferred that R¹⁰, R¹¹, R¹², R¹³, are each hydrogen; or one or more of R¹⁰, R¹¹, R¹², R¹³ are methyl, fluoro, trifluoromethyl,

methoxy, or dimethylamino; or where R¹⁰ and R¹¹ are joined to form a benzene ring and R¹² and R¹³ are each hydrogen (thus forming a naphthyl group with the existing phenyl ring).

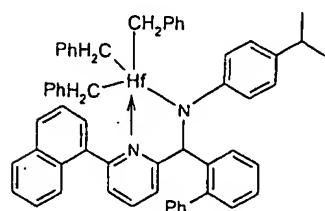
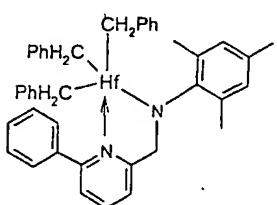
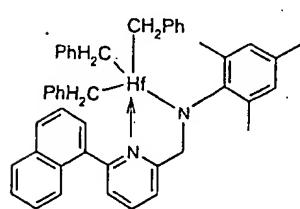
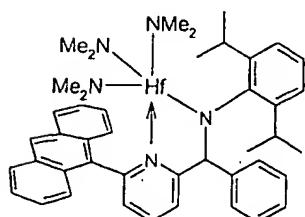
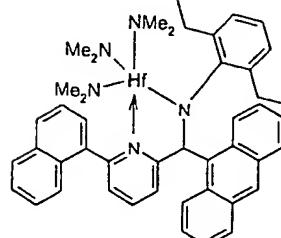
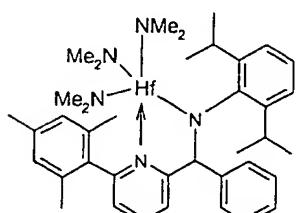
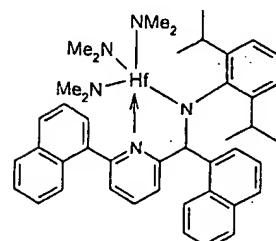
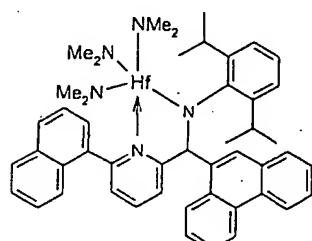
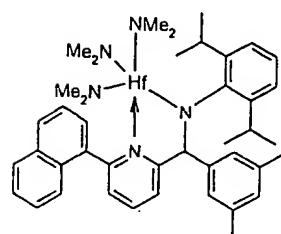
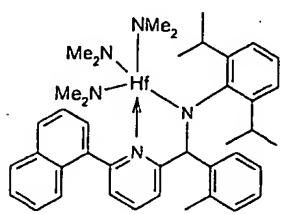
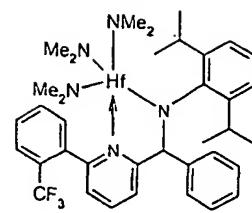
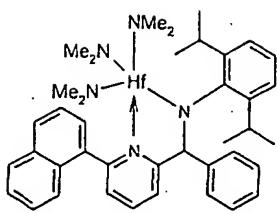
[0098] Specific 2,1 and 3,2 metal complexes that are useful for the production of
5 isotactic polypropylene include:

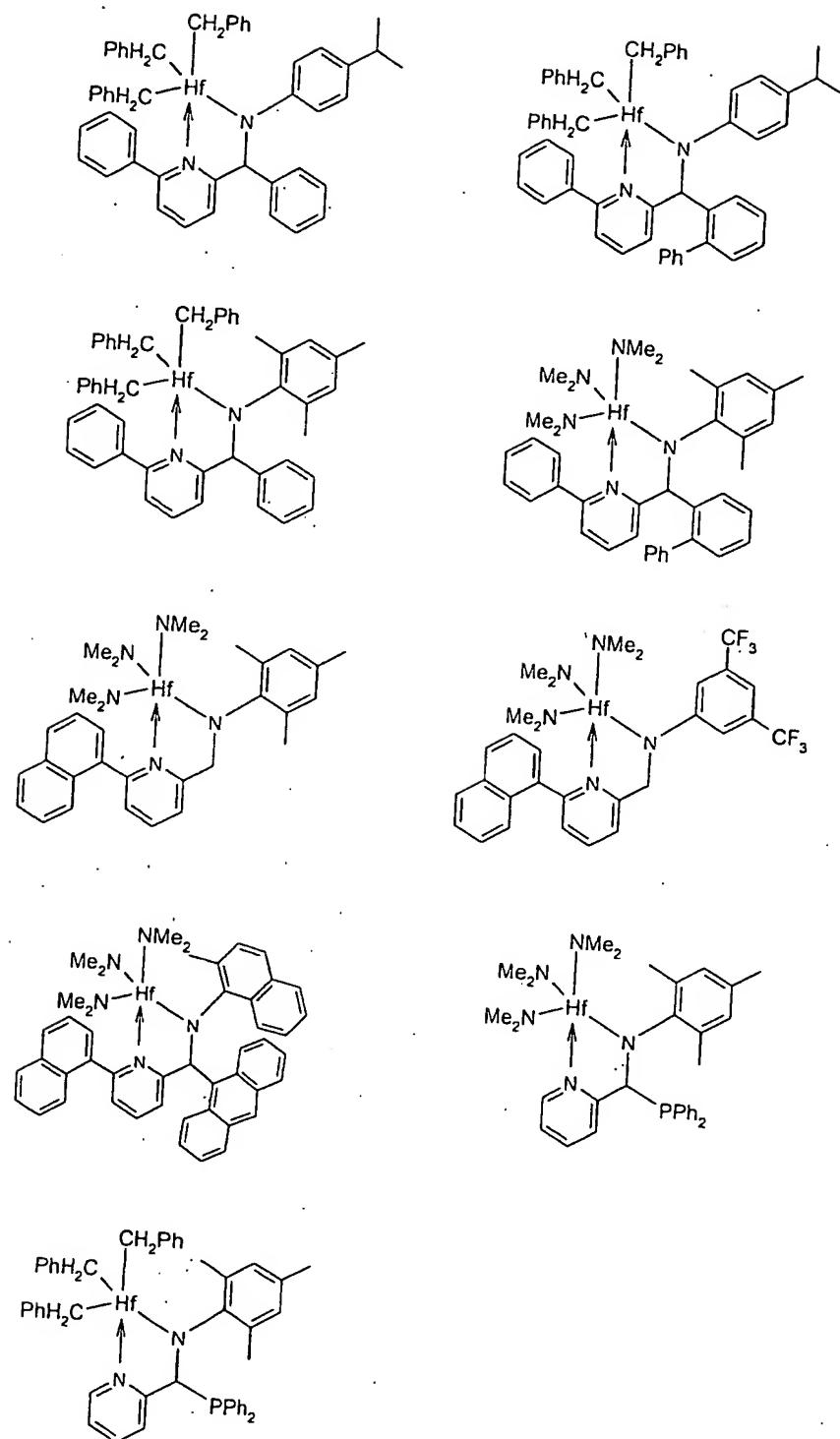


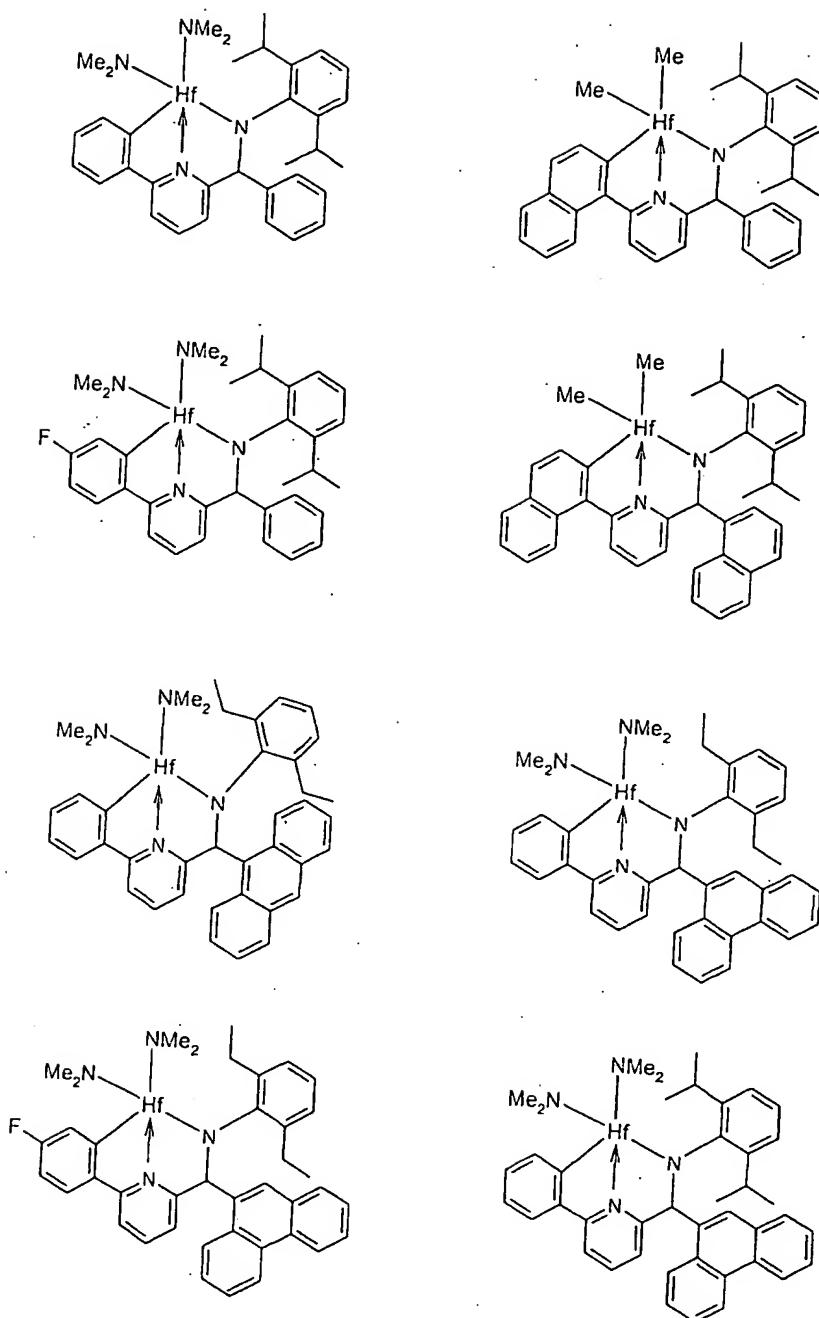


[0099] For the production of ethylene-styrene copolymers, there are different preferences depending on the type of polymer that is desired. In some embodiments, it is preferred that the above formulas for complexes are used, particularly with R^7 selected from the

group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Specific 2,1 and 3,2 complexes that are preferred for ethylene-styrene copolymer production include:







[0100] For the production of ethylene-1-octene copolymers, it is preferred that the metal complexes of the above general formulas are used, with either or both of R^3 and/or R^7 being independently selected from the group consisting of aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Specific 2,1 and 3,2 metal complexes that are preferred for ethylene-1-octene copolymer production include:

